



For Reference

NOT TO BE TAKEN FROM THIS ROOM

THE CATALYTIC DECOMPOSITION OF ETHYL
ALCOHOL AND CATALYTIC REACTIONS OF WATER
GAS MIXTURES UNDER PRESSURE

- by -

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University of Alberta
Department of Chemistry,
April, 1931.

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This is to certify that the undersigned have read and recommend to the Committee on Graduate Studies for acceptance, a thesis submitted by Herbert E. Morris, B. Sc., entitled:

I. "The decomposition reactions of ethyl alcohol, ethyl alcohol and carbon dioxide, and ethyl alcohol and water mixtures over catalysts,

- and -

II. "A study of the reactions of carbon monoxide, carbon dioxide and hydrogen mixtures over catalysts at high pressure and elevated temperatures".

Professor

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- I. The decomposition reactions of ethyl alcohol, ethyl alcohol and carbon dioxide, and ethyl alcohol and water mixtures over catalysts.

- and -

- II. A study of the reactions of carbon monoxide, carbon dioxide and hydrogen mixtures over catalysts at high pressure and elevated temperatures.

Herbert E. Morris.

A C K N O W L E D G M E N T.

I wish to take this opportunity of thanking all of those who have assisted materially in the completion of this work.

- To Dr. E. H. Boomer, who directed the research and whose valuable suggestions, admirable patience and kindly criticism, made the attainment of the objective possible.

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- To the Research Council of Alberta and the National Research Council of Canada, whose financial assistance made the project possible.

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Herbert E. Morris.

C O N T E N T S.

Part I.

Page

GENERAL INTRODUCTION

Statement of problem and methods of investigation	1
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Part II.

THE CATALYTIC DECOMPOSITION OF ETHYL ALCOHOL, ETHYL ALCOHOL AND CARBON DIOXIDE, AND ETHYL ALCOHOL AND WATER MIXTURES.

1. Introduction	6
2. Literature review	8
3. Experimental technique, apparatus, analytical methods	16
4. Experimental results	24
Various catalysts	27
Nickel-chromium catalysts	67
5. Discussion	100
Formation of ethane	101
Formation of methane	106
Formation of carbon dioxide	118
6. Conclusions	126

Part III.

THE REACTIONS OF CARBON MONOXIDE, CARBON DIOXIDE AND HYDROGEN MIXTURES OVER CATALYSTS AT HIGH PRESSURE AND ELEVATED TEMPERATURES.

1. Introduction	127
2. Literature review	
Methanol synthesis	128
Synthesis of other organic compounds	132
3. Experimental technique	
Preparation of gas mixtures	140
Apparatus, analytical methods	142
4. Experimental results	149
5. Summary	160

PART IV. BIBLIOGRAPHY

161

P A R T I.

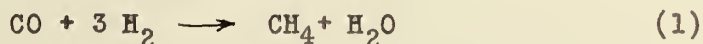
GENERAL INTRODUCTION

There is in the Province of Alberta an enormous supply of natural gases of great potential value, but because of present economic and social conditions, of little immediate use. In any comprehensive survey of possible chemical processes that could utilize natural gases as raw material, the chemistry of water gas and like mixtures has an important part.

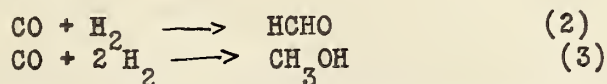
Carbon monoxide and hydrogen or carbon dioxide and hydrogen mixtures are readily and cheaply produced from the simple saturated hydrocarbons that make up natural gases. As is well known, these gaseous mixtures are reactive and may produce a variety of liquid and gaseous organic compounds with the help of suitable catalysts and proper conditions of temperature and pressure.

The following dissertation is a contribution of a specialized nature to this latter field.

The possibilities inherent in the water gas mixture have been obvious since Sabatier and Senderens first reduced carbon monoxide to methane.



It is evident that, although these workers were unable to obtain any additional products, at least two other reactions should be possible.



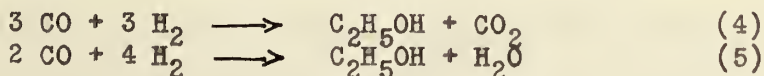
However, it was not until 1913 that the Badische Anilin und Soda Fabrik patented a process whereby a wide variety of catalysts, at a temperature of 360-420°, converted ordinary water gas, under a pressure of over 100 atmospheres, into a complex mixture of hydrocarbons, alcohols, and other oxygenated compounds. Methyl alcohol was indicated as one of the most prominent constituents.

A patent issued to Patart in 1921 claimed high yields of methanol by passing a mixture of 2 volumes of hydrogen and 1 volume of carbon monoxide at high pressure and about 400°C over a zinc oxide catalyst. Since that time a great number of patents have been issued covering the synthesis of methanol from water gas mixtures and carbon dioxide - hydrogen mixtures. The general tendency seems to show that a catalyst containing zinc and chromium oxides, preferably in the form of the basic zinc chromate, is the most active for the alcohol synthesis from water gas mixtures. The reaction occurs satisfactorily at 350° under a pressure of 100 atmospheres.

The possibilities of forming a large number of other

organic compounds were not overlooked and Fischer and his co-workers soon announced the formation of Synthol by the reduction of carbon oxides under pressure. This work was started in the quest for other sources of motor fuels, with catalysts containing iron and alkali proving the most successful. The actual constituents of Synthol are present as a complex mixture of hydrocarbons and oxygenated organic compounds, with ethyl alcohol forming an unexpectedly small portion of the alcohol content. The products consist of relatively large quantities of isobutyl, and higher alcohols up to C_9 , aliphatic acids up to C_9 , as well as aldehydes, ketones and esters in small quantities. The ratio of hydrocarbons to oxygen containing compounds varying considerably with results, not being reproducible within rather wide limits.

The fact that ethyl alcohol has not been found in an appreciable quantity among the products of this reaction indicates either that catalysts have not been found which will promote the formation of this alcohol, or that the catalysts in use are too active and carry the reactants through the ethanol stage to higher alcohols. There are two water gas reactions yielding ethyl alcohol directly

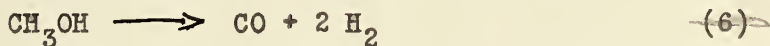


It is rather difficult to imagine the reactants coming together

in these ratios but the possibility of a step-wise formation certainly exists and will be discussed in Part III.

There are two general methods of investigation of these reactions having catalyst testing as their objective. The first method, which is rather cumbersome, involves the passage of the gaseous mixtures over catalysts under pressure and the determination of the products and extent of any reactions. This method gives direct unequivocal information on the efficiency of the catalyst in promoting the desired reaction.

The second method which was suggested by Patart involves the decomposition of the desired product over the catalyst being tested and examination of the products of this reaction. The principle that a catalyst promotes both forward and reverse reactions in a chemical equilibrium is tacitly assumed. As an illustration, a catalyst that promotes exclusively, the reaction



may be expected to promote in some degree at least, the reverse reaction rather than other possible reactions. This method has been vigorously pursued by Frolich and co-workers, and is a general method of catalyst testing in vogue today. It has actually been shown experimentally that, with a reasonable degree of latitude, a catalyst which promotes the decomposition of methanol to carbon monoxide and hydrogen will also promote the formation of methanol from these gases under pressure. Both

methods have been used in the work herewith reported, reactions ~~(4) and (5)~~ being investigated in both directions with a variety of catalysts under different conditions. Such studies have as an objective, apart from contributing to the subject of catalysts, the possibilities of synthesis of ethyl alcohol by the hydrogenation of carbon oxides. Their practical relation to the basic problem, the chemical utilization of natural gas, is clearly evident upon consideration of the enormous market enjoyed by ethyl alcohol as compared to methyl alcohol.

P A R T I I.

I N T R O D U C T I O N.

The catalytic decomposition of ethyl alcohol has been quite extensively investigated for several reasons. Due to the fact that it may undergo decomposition reactions involving either dehydration or dehydrogenation, it is a satisfactory compound for the determination of the specific nature of the activity of a catalyst. Similarly it is a most prolific source of information in investigations dealing with the mechanism of catalysis.

While the decomposition of alcohol with single metal catalysts, or with the addition of small quantities of promoters, has been rather thoroughly investigated, there is very little work reported on the action of binary mixtures of catalysts. The majority of the catalysts studied in this work are of this latter class. Results of the work are therefore given in a detailed manner because they offer a comprehensive study of the reactions of ethyl alcohol over a wide range of mixtures of catalysts.

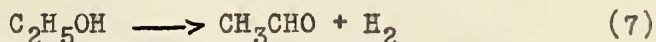
Recent work on the mechanisms of catalytic reactions indicates that in many cases the reactants do not follow the most obvious routes to the final product; rather, the final products are the result of several consecutive reactions, and the factors

influencing these reactions must be considered. Moreover, the existence of concurrent or side reactions frequently add to the complexity of the happenings over the catalyst. Some results on the decomposition of ethanol have shown that secondary reactions quite frequently occur leading to the formation of a variety of products other than can be due to single dehydrogenation or dehydration. From the results obtained in this study the conclusion has been reached that the catalytic decomposition of ethyl alcohol is a complex phenomenon in which the products of primary dehydrogenation or dehydration readily undergo a number of secondary reactions. The simple dehydration and dehydrogenation reactions have been observed but the secondary formation of ethane, methane, carbon dioxide, and acidic condensates, previously noted by other investigators, has been confirmed and the reactions leading to these products have been more thoroughly examined.

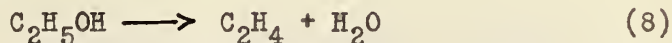
Literature Review.

The following review of previous work is not complete but will serve to indicate the general methods in use in this type of work and outline the nature of the results to be expected. It is believed that no important contribution has been neglected. Many of the more relevant references have been reserved for the discussion of the results.

In 1884 Maquenne (15) noticed that the products of the pyrogenic decomposition of ethyl alcohol at dull red or bright red heat contained a variety of gases which indicated far-reaching decomposition of the alcohol. These included hydrogen from the reaction



and ethylene from the reaction,



These two reactions dehydrogenation and dehydration are the two main ways in which ethyl alcohol is decomposed.

Nef (17) working at 590-640° found very similar results, and also noted methane and carbon monoxide as products of the decomposition of the acetaldehyde produced by reaction (7)



Ipatiev (16) investigated the reactions in glass and platinum tubes and found that in the latter, reaction occurred

at a considerably lower temperature and was largely dehydrogenation, while the presence of zinc in the reaction tubes lowered the temperature still further.

Greene (20) had noticed in 1878 that dropping ethyl alcohol on hot ZnCl_2 produced a variety of products including hydrogen and ethylene, and Jahn (23) found that upon passing alcohol over zinc dust at dull red heat, dehydrogenating action was complete, and at 300-350° the products included both hydrogen and ethylene.

This latter work marks the first catalytic decomposition at temperatures below 400° and was probably the first work on the actual catalytic decomposition of ethyl alcohol.

Following closely the work of Ipatiev came the classical researches of Sabatier who, with his two assistants, Senderens and Mailhe, laid comprehensive foundations for the study of catalytic organic chemistry.

The investigations of a wide variety of metallic and metallic oxide catalysts followed in succeeding years and ethyl alcohol was a favorite substance for study.

In what follows, a brief summary of the nature of the action of the catalytic metals is given and references in the bibliography indicate the sources of additional information. With regard to the dehydrating catalysts it should be noted that two products are possible, partial dehydration to give ethyl ether, and complete dehydration to ethylene. The temperatures used in

this work, however, preclude the formation of the former substance.

The following table, due to Rideal and Taylor (2) summarizes the work of Sabatier and Mailhe (26) on the action of metallic oxides on primary alcohols. The figures refer to the percentage of ethylene in the ethylene-hydrogen gas mixture produced by the passage of alcohol vapor over the catalyst mass at about 350°.

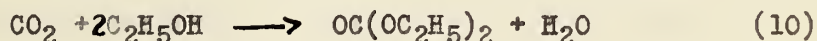
ThO ₂	100)	
Al ₂ O ₃	98.5)	Dehydration Catalysts
W ₂ O ₃	98.5)	
Cr ₂ O ₃	91)	
SiO ₂	84)	
TiO ₂	63)	
BeO	45)	Mixed Dehydration and
ZrO ₂	45)	dehydrogenation catalysts.
U ₃ O ₈	24)	
Mo ₂ O ₅	23)	
Fe ₂ O ₃	14)	
V ₂ O ₃	9)	
ZnO	5)	
MnO ₂	0)	
SnO	0)	
CdO	0)	
Mn ₃ O ₄	0)	Dehydrogenation catalysts.
MgO	0)	
Cu	0)	
Ni	0)	

Many other catalysts were studied by the early workers but this will suffice as indicative of the general nature of the catalytic decomposition of ethyl alcohol.

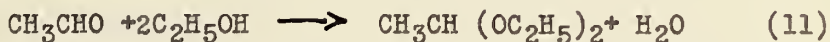
Since this work, however, there have been many more recent papers on the catalytic decomposition of ethyl alcohol with

various ends in view. The elucidation of mechanisms, finding optimum decomposition conditions, comparison of catalytic activities, examination of promoter effects and most satisfactory methods of preparing catalysts, have all received much attention. Among these should be mentioned the investigations of Palmer, Constable, Rideal, Armstrong and Hilditch, Adkins and co-workers, Brown and Reid, Alvarado, Cremer, Engelder, and others. The specific results obtained in some of these papers will be referred to in the course of later discussions.

The possibility of reaction between carbon dioxide and ethyl alcohol was investigated by Gilfillan (56) who wished to produce a diethyl carbonate using thoria catalysts.



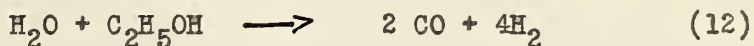
No indication of this reaction was obtained, however, although the carbon dioxide seemed to promote the formation of acetal as follows:



The decomposition of mixtures of alcohol and water using a nickel catalyst has been reported in two papers. Armstrong and Hilditch (47) found that with water and alcohol in solutions the secondary decomposition of acetaldehyde produced by dehydrogenation was appreciably retarded up to 335°C. Water apparently improved the yield of aldehyde with reference to hydrogen produced.

With a given concentration of reactants, as the temperature is raised the yield of aldehyde is lowered, although the amount of alcohol decomposed and the quantity of hydrogen produced is much increased. At higher temperatures the yield may be partially restored by using more water. The other products include butyraldehyde, crotonaldehyde, and ethyl acetate such as are produced in the decomposition of acetaldehyde itself. The action of the water in these experiments is essentially that of an anticatalyst in retarding the decomposition of the aldehyde.

No mention is made of the possibility of the reverse of reaction (5), that is

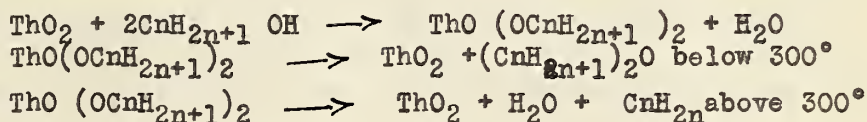


Russel and Marschner (46) studied the reaction below 200° to prevent the decomposition of the aldehyde. They confirmed the previous workers by finding that water increased the amount of alcohol undergoing reaction and decreased the percentage of aldehyde decomposed.

In connection with the catalytic decomposition of ethyl alcohol, several theories have been advanced to account for the catalytic activity of metallic interfaces, and some of these seem worthy of preliminary consideration at this point. The well known theories of catalysis involving intermediate compound formation, and adsorption may be found elsewhere (1, 2, 7, 8).

They will not be discussed here except to illustrate the application of the intermediate compound theory to the dehydration of alcohol over thoria by Sabatier and Mailhe (26).

The mechanism is self-explanatory and is represented by the scheme



Adkins (34) believes that the activity of a catalyst depends on the molecular size of the cavities in the mass and illustrates this by preparing an alumina catalyst in seven different ways and obtaining markedly different results. With Nissen (35) he repeats the above and states that selective adsorption is not the cause of reactions. Adkins and Lazier (36a) find little relationship between factors determining the amount of material undergoing reaction and those determining the paths which the reaction follows. They advance three hypotheses to account for these different reactivities; (1) the relative adsorbing powers of the catalyst, (2) the variation in the spacing of the active points of the catalyst, and (3) the difference in degree of unsaturation of the atoms of the catalyst.

Constable (31) states that reaction occurs only when the alcohol molecule is adsorbed over a characteristic arrangement of metallic atoms, called a reaction centre, and, since a surface

exposes many crystal faces as well as some inactive material, it is evident that there is a large variation in the number of atom centres lying beneath one adsorbed molecule. The relative density of these reaction centres will also vary and these differences in surface activity per unit area will account for some of the periodic variations in the activity of a catalyst. He also advanced the theory (31a) that decomposition occurs when the alcohol molecule possesses an energy above the quantity characteristic of the temperature of the film and since only the $\text{-CH}_2\text{OH}$ group is changed it is therefore possible that this excess energy called the energy of activation must be present in this group.

Hoover and Rideal (33) in noting the simultaneous dehydrating and dehydrogenating activity of thoria, conclude that these two reactions are promoted by different areas or patches on the surface of the catalyst. They seem to obtain support for this theory from the different energies of activation and the phenomenon of selective poisoning, the reactions apparently proceeding on active patches which vary in their adsorptive capacity.

Russel and Marschner (46) advance the theory that the presence of water in alcohol cuts down the time which the molecules spend on the catalytic surface; this effect being most prominent with the aldehyde. They conclude that nickel catalysts possess areas of various activities. The most active portions adsorb poisons which diminishes their activity, and the action

proceeds on the less active areas. To explain the protective effect on aldehyde decomposition of relatively small concentrations of water they attribute to this water a specific effect which probably involves its preferential adsorption. This effect apparently leaves more of the active areas free to function and hence increases the total activity of the catalyst.

EXPERIMENTAL TECHNIQUE.

Apparatus.

The apparatus used in these experiments is illustrated in Plates I, II and III. The initial arrangement is illustrated in figure 1. A is a calibrated reservoir from which the alcohol passed through a stopcock to a drop counter B and thence into a pyrex glass chamber electrically heated by a furnace F. Here the liquid was vaporized and passed over the catalyst C, held in position by asbestor fibre plugs. This arrangement results in a uniform temperature throughout the catalyst and ensures equality of vapor and catalyst temperature. The liquid products were collected in a water cooled condenser and another large condenser acted as a trap for oil fumes and vapors hard to condense. From here the gases passed through a flowmeter, and a water bubbler to a Sargent wet test meter, filled with a mineral seal oil, where the total gas volume was recorded. The furnace, F, was wound with #20 gage nichrome wire and temperatures were measured with a calibrated platinum-platinum rhodium thermocouple using a Leeds and Northrup potentiometer indicator.

This method of controlling the rate of alcohol flow was rather unsatisfactory and space velocities were difficult to duplicate. A further source of trouble was the temperature difference between the entering liquid and the furnace, which caused frequent cracking of the glass just at the point of contact.

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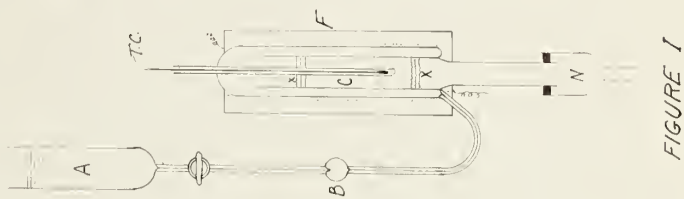


FIGURE 1

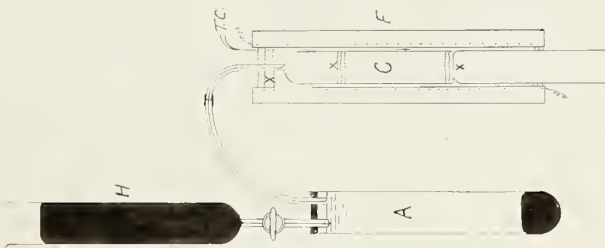


FIGURE 2

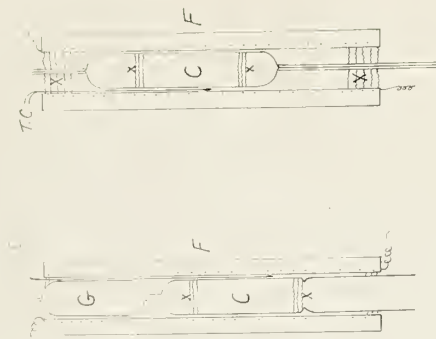


FIGURE 3

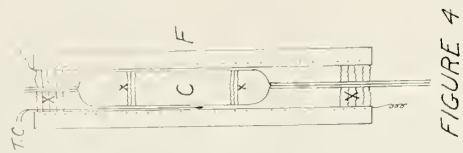


FIGURE 4

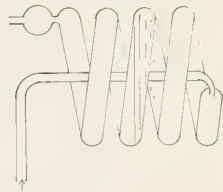


FIGURE 5

The second form of apparatus, figure 2, was a modification of the method of Adkins and Nissen (35a) in which mercury, in a calibrated reservoir, H, was admitted through a stopcock into an alcohol reservoir, A, which forced the liquid through a capillary into the reaction chamber, C. The furnace F consisted of a porcelain tube wound with nichrome and insulated with asbestos cement. It was found that using a furnace of this type the temperature of the wall of the reaction tube was practically the same as that of the catalyst mass, except at the first instant of contact between the alcohol and the catalyst, when a sharp rise of temperature occurred. The temperature readings with the thermocouple placed outside of the tube are within 5° of that of the catalyst mass. The reaction tube was again made of pyrex glass and the condensing and measuring system the same as that previously outlined.

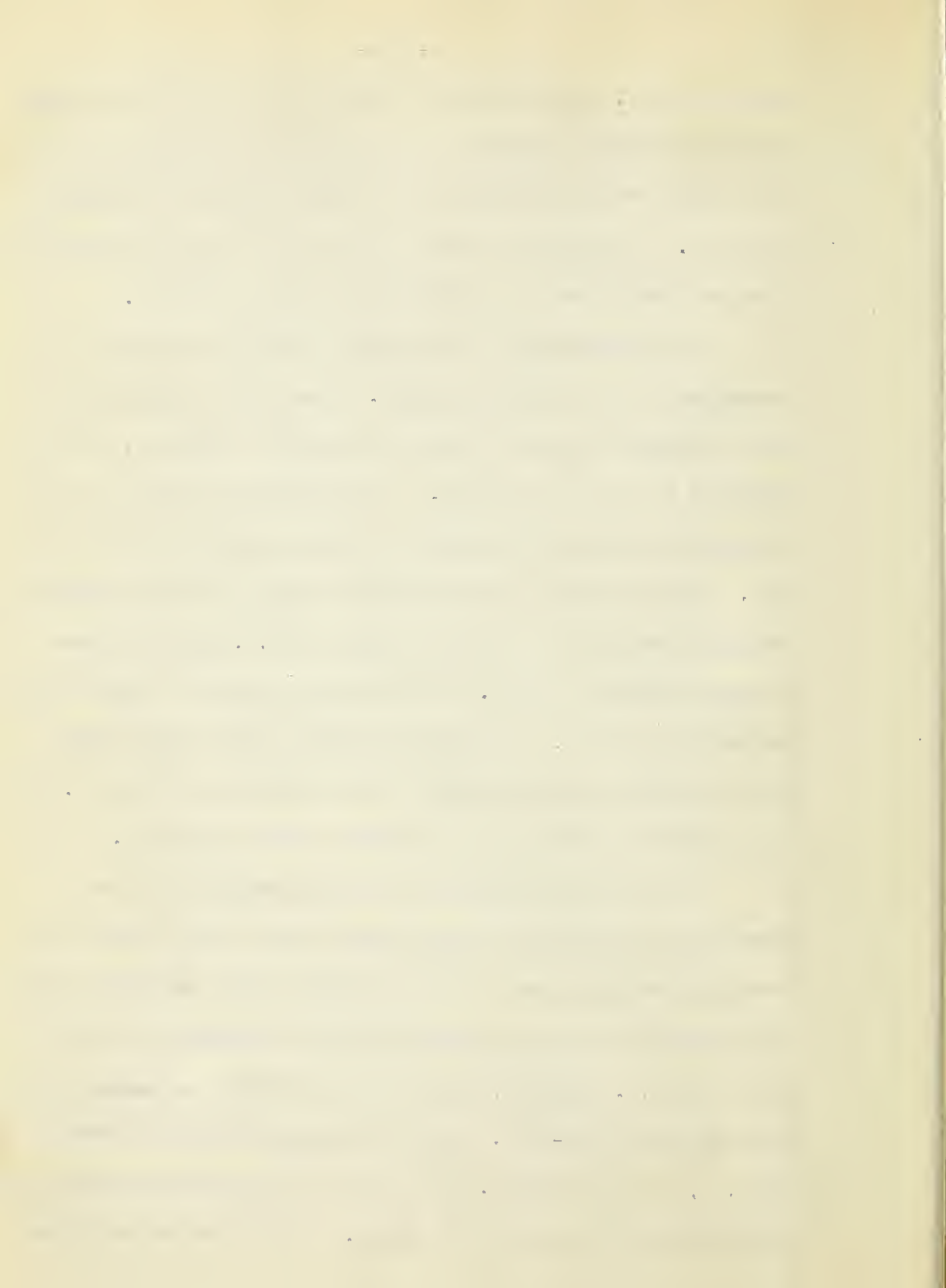
A slight modification of the reaction chamber is illustrated in figure 3, where an expansion chamber, G, was used to ensure complete vaporization of the liquid before coming in contact with the catalyst. Results were much the same with this device as with the previous tube and it seems probable that with a relatively slow rate of flow, vaporization was complete in the original arrangement.

In some of the experiments the quantity of condensate was very small and it collected on the wall of the lower part of the

reaction tube. To obviate this difficulty and provide a rapid and more complete removal of the products of decomposition, a capillary tube was sealed to the reaction chamber as shown in figure 4. This ensured removal of the liquid from the reaction zone and facilitated the collection of these products.

The experiments using carbon dioxide and alcohol were conducted in the following manner. Commercial carbon dioxide from a cylinder passed through a flowmeter, a bubbler, and was measured in a wet test meter. A considerable quantity of CO_2 was passed through this system to ensure saturation with the gas. From the meter the gas passed through a Calcium chloride drying tower and into a coil of about 40 c.c. capacity containing absolute alcohol. This coil was placed in a water bath maintained at 65°C . The CO_2 containing alcohol vapor passed into a reaction chamber such as that indicated in figure 4, and the products collected in the manner already described.

With liquid reactants of varying composition, the necessity of vaporizing these liquids before they reached the catalyst was recognized and the apparatus which satisfied this requirement is shown in figure 6, where K represents a bulb of about 250 c.c. capacity, placed in an oil bath, J, heated to a temperature of $105\text{-}110^\circ$. The vapors passed through a heated tube, L, to the catalyst. This type of vaporization proved very efficient and was easily controlled. A modification to adjust



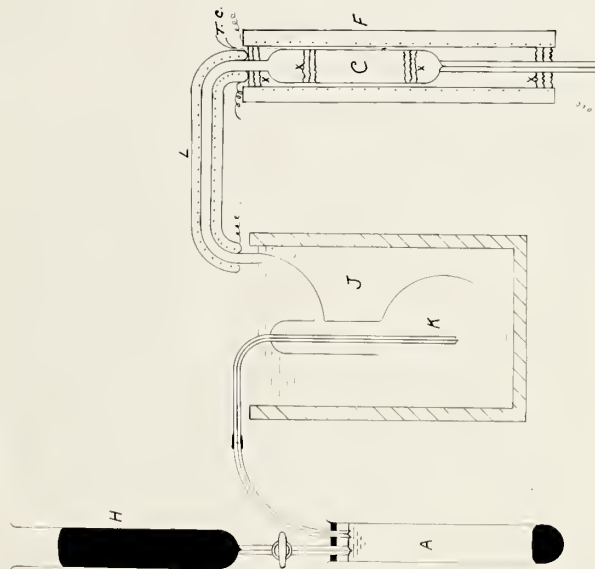


FIGURE 6

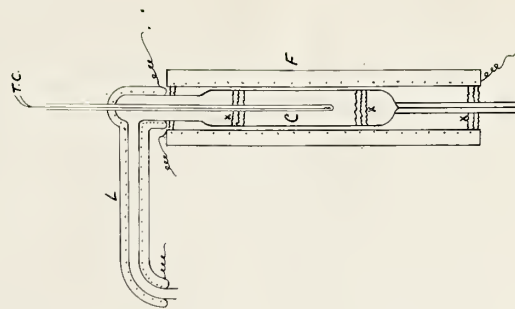


FIGURE 7

the pressure built up within this vaporizing bulb involved a needle valve which could be easily regulated to control the rate of flow of vapor over the catalyst.

The installation of a split, multiple unit electric furnace to replace the heater previously described necessitated remodelling the catalyst chamber to provide inside temperature readings, where the thermocouple would not be influenced by direct radiation. This new set up is shown in figure 7, and the thermocouple well marks the only deviation from the older arrangement.

As a result of this work a new apparatus for the study of catalytic decompositions has been developed and is illustrated in figure 8. Mercury from a burette, H, forces the alcohol in A into the vaporizer, K, from which it passes over the catalyst, C. A reflux condenser, M, cools the vapors which pass through a water cooled condenser, N, into P, a water-jacketted burette. The volatile portion passes into Q, a condenser placed in a mass of CO_2 and alcohol contained in a Dewar flask, R. This removes the remaining condensable vapors and the gas, which may be sampled at S, passes through a flowmeter T, into a water bubbler, and the volume determined in a wet test meter.

This apparatus was the culmination of this part of the

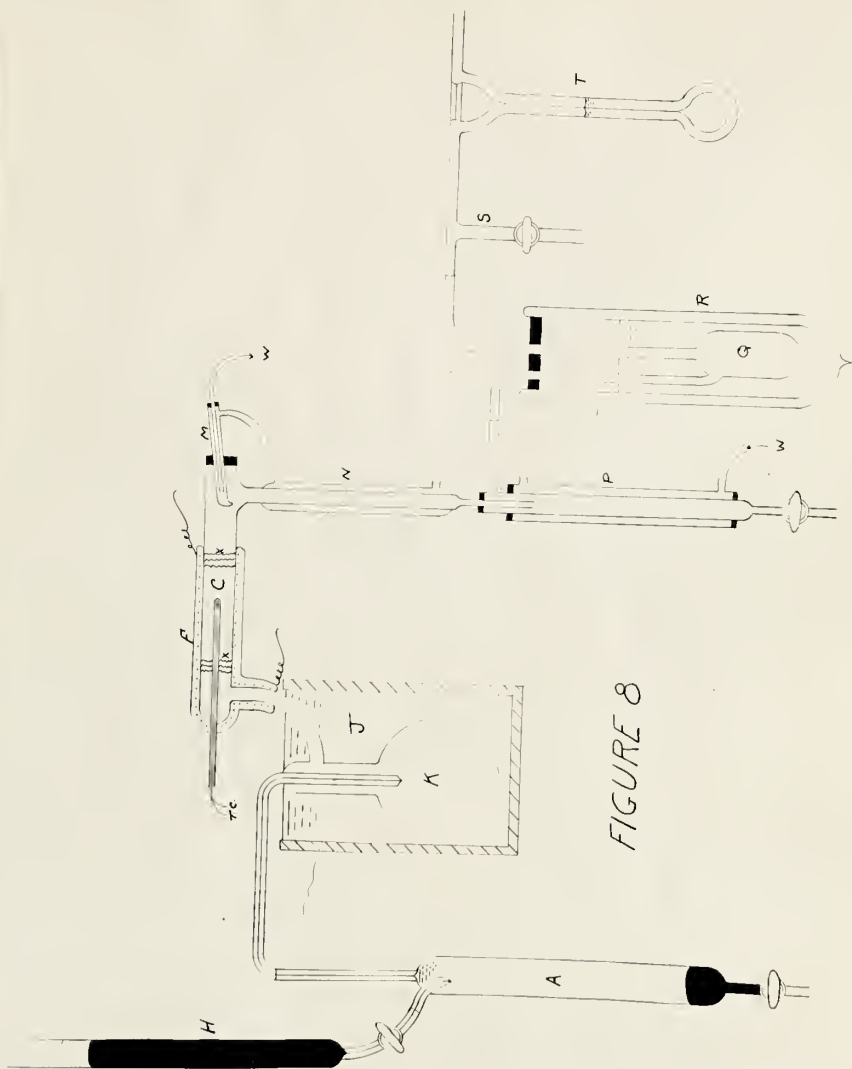


FIGURE 8

research, and most of the work reported in this dissertation was completed on the other equipment, but the benefits derived from this work are evident in this final piece which has a great number of obvious advantages over many other types of apparatus recommended for this work, and it should prove acceptable for any other similar study of catalytic decomposition where a compact and convenient set-up is required.

Analytical Methods.

The products of these reactions were extremely complex in both gaseous and liquid state. The analysis of the gaseous products was carried out initially in an improved Orsat apparatus and later on an improved Bureau of Mines apparatus. In both cases, carbon dioxide was determined by absorption in KOH, ethylene in fuming sulfuric acid and oxygen in alkaline pyrogallol. Hydrogen and carbon monoxide were determined by combustion over CuO at 300°, and methane and ethane measured by slow burning with oxygen in contact with a hot platinum wire.

The liquid products were very complex and difficult to analyse even qualitatively. Several sizes of fractionating columns were used for general separation, and in a few cases the micro-fractionating apparatus of Cooper and Fasce (152) was employed. Various qualitative tests for acids, aldehydes, etc. were used and will not be discussed here. In the cases of oil

formation, where a sample of reasonable size could be obtained, a combustion analysis was made. Even in these cases the analyses indicated that the substance was frequently a mixture.

EXPERIMENTAL RESULTS.

The actual experimental results will be presented in detail, but it seems advisable to discuss the general results at this stage to emphasize certain features which are indicated with some of the catalysts. Three general types of decomposition are evident in all reactions whether ethyl alcohol is used alone, with water, or with carbon dioxide. As would be expected, two of these, dehydration and dehydrogenation, are evident in many cases, but unexpectedly large amounts of CO_2 in the exit gases make a decarboxylation reaction quite apparent. The mechanisms by which this gas might be formed will be discussed later, but its prevalence should be noted with specific catalysts.

The results are arranged on the basis of catalyst numbers and this gives rise to an apparent irregularity in experimental order. It should be pointed out that this series of catalysts was started previously for another line of research, and the catalysts were not used in numerical order in the work reported here. This accounts for the absence of certain members in the catalyst series and the frequent change of reactants indicated in the results.

This method of presentation has been deemed preferable for numerical continuity and conservation of space, since some of the results are cited in several points of discussion and are referred to by means of the table number only. Specific points

are noted with individual catalysts, but the general discussion has been reserved until all results have been presented.

In particular the formations of carbon dioxide, methane and ethane are examined, with references both to previous work and that reported here, following the complete presentation of results.

This research was instigated primarily to study the gaseous products of decomposition and consequently the liquid products have not been examined in the majority of cases. Where indications of unusual results were obtained, however, an investigation of the condensate was made, both qualitatively and quantitatively. The nature of the majority of these condensates is such that a complete analysis is extremely difficult to make and detailed results have not been obtained.

With regard to the experimental details; except where noted the catalysts were reduced in situ at 300° by a stream of hydrogen for at least four hours, or until no further formation of water was evident. The actual period of reduction varied considerably with the catalysts.

The tables are believed to be self-explanatory. The row, "Theoretical CO₂ percentage in gas", refers to the volume of CO₂ gas used compared to the total gas volume obtained in the experiment. That is

$$\frac{\text{Volume of CO}_2 \text{ used}}{\text{Total gas volume obtained}} \times 100 = \text{Theoretical CO}_2 \text{ percentage in gas.}$$

The catalytic or pyrolytic effect of the reaction chamber itself was examined by passing a large volume of alcohol, at a slow space velocity, through the empty tube at 450° using CO₂ to obtain a minimum space velocity. There was practically no reaction; the condensate volume being equal to that of the alcohol passed through. The gas contained 98.6% CO₂, 0.9% H₂ and 0.5% C₂H₄. This small decomposition was expected under these conditions and is in agreement with other results on the pyrolysis of ethyl alcohol. It is evident that this reaction would be even smaller with a higher rate of alcohol flow similar to that used with alcohol or alcohol and water mixtures. The possibility of the asbestos plugs having catalytic activity was recognized and using the conditions mentioned previously it was found that at 350° the reaction was barely perceptible, and the gaseous products contained 96.5% CO₂, 2.2% H₂ and 1.3% C₂H₄. At 450° the gas consisted of 90% CO₂, 8% H₂ and 2% C₂H₄. This apparent activity was not unexpected under these conditions but would not be evident when a catalyst was in the chamber, unless such a catalyst was relatively inert.

Catalyst number 12.

Long fibre asbestos soaked in a concentrated solution of $\text{Ni}(\text{NO}_3)_2$ and the resulting mass dried and ignited in an electric muffle furnace.

Ethyl alcohol and water were studied using apparatus shown in fig. 1. The results are shown in table 1.

T A B L E I.

Temp. °C	330	375	400	450	500
Liquid used in c.c.	69	-	19	16	23
Rate of flow cc/min.	0.11	-	0.07	0.10	0.07
Condensate c.c.	10	-	2	2	6
Gas yield in litres	11.7	-	2.8	2.0	8.3
Gas flow cc/min.	19.5	-	10.2	13.1	26.7

Gas Analysis

CO_2	0.8	19.5	21.8	23.4	20.6
C_2H_4	nil	nil	nil	nil	nil
H_2	40.9	30.0	24.7	23.6	31.2
CO	25.7	5.5	3.4	4.4	2.0
CH_4	28.6	42.5	50.0	48.6	45.2
C_2H_6	4.0	2.5	nil	nil	nil

The liquid samples were not saved.

The catalyst was badly carbonized indicating decomposition of CO , and there is also rather convincing evidence that all of the methane present was formed by aldehydic decomposition.

Catalyst number 16.

An equimolecular mixture of ZnO and Cr_2O_3 triturated with water and dried at 110° .

Carbon dioxide and alcohol were studied in the described manner. The results are shown in table 2.

T A B L E 2.

Temperature $^\circ\text{C}$	450	450
Liquid used in c.c.	9	5
Condensate in c.c.	7	2
CO_2 volume in litres	0.56	3.3
CO_2 flow in cc/min.	50	25
Total gas yield in litres	1.06	7.1
Theoretical CO_2 percentage in gas	52.8	46.7

Gas Analysis

CO_2	50.2	50.0
C_2H_4	2.5	2.9
H_2	35.6	35.3
CO	7.5	9.0
CH_4	nil	nil
C_2H_6	4.3	2.7

A mist forms in the exit gases which condenses in the second receiver.

The ethane formation will be discussed later. The lack of methane concurrent with appreciable amounts of CO is unexpected and suggests that the decomposition of acetaldehyde is not the source of carbon monoxide.

Catalyst number 22.

A complex mixture containing 4 moles of Cr_2O_3 , 1 mole of ZnO , $\frac{1}{2}$ mole of Al_2O_3 , and a trace of Cu powder. The components were mixed into a paste using NaOH and dried at 110° .

Alcohol and water were investigated in apparatus 1. The results are shown in table 3.

T A B L E 3.

Temperature $^\circ\text{C}$	400	450	500
Liquid used in c.c.	20	23	35
Rate of flow cc/min.	0.06	0.1	0.08
Condensate c.c.	18	13	11
Gas yield in litres	2.8	10.3	28.35
Gas flow cc/min.	8	45	62

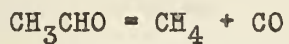
Gas Analysis

CO_2	9.2	8.7	14.7
C_2H_4	2.3	4.9	3.8
H_2	88.6	85.5	77.8
CO	nil	nil	trace
CH_4	nil	1.0	3.6
C_2H_6	nil	nil	nil

There was a persistent mist which did not settle out in the condenser and was apparently an oil. The condensate was in two layers, about one quarter oil and the rest largely water. Reducing the rate one half, stopped the mist formation but oil still formed.

This is evidently a case in which a decarboxylation reaction is occurring. Dehydrogenation occurs in large amounts which would lead to acetaldehyde. The lack of CH_4 and CO

among the gaseous products indicates that the reaction



is not proceeding and the CO_2 cannot come from a CO decomposition.

This is further proven by the absence of carbon on the catalyst.

Catalyst number 24.

A mixture of 1 mole of Cr_2O_3 , 1 mole of ZnO , and $\frac{1}{2}$ mole of CuO , with a trace of Cu powder to promote reduction. The components were ground together in water and dried at 110° .

With alcohol and water the results are shown in table 4, and with alcohol and CO_2 the results are shown in table 5.

T A B L E 4.

At 350° - 400° the catalyst was inactive with the solution passing over unchanged.

Temperature $^\circ\text{C}$	450	500
Liquid used in c.c.	19	49
Rate of flow cc/min.	0.11	0.11
Condensate c.c.	17	25
Gas yield in litres	3.1	28.4
Gas flow cc/min.	19	58

Gas Analysis

CO_2	7.3	10.6
C_2H_4	3.5	3.5
H_2	89.2	86.0
CO	nil	nil
CH_4	nil	nil
C_2H_6	-	-

The results here are very similar to those of the previous catalyst #22, which differs mainly in being alkaline.

T A B L E 5.

Temperature $^\circ\text{C}$	450	350	450
Liquid used in c.c.	6	6	4
Condensate c.c.	2	5	3
CO_2 volume in litres	3.88	4.70	3.56
CO_2 flow cc/min.	50	50	50
Total gas yield in litres	6.15	4.76	7.0
Theoretical percentage CO_2 in gas	63.2	98.5	51.0

Table 5 - continued.

Gas Analysis.

CO ₂	61.8	79.2	51.0
C ₂ H ₄	2.6	0.6	1.8
H ₂	33.3	14.6	36.5
CO	nil	nil	1.6
CH ₄	nil	nil	nil
C ₂ H ₆	2.3	5.5	9.1

Catalyst appears unchanged.

This is one of the first results using CO₂ and indicates a feature which is very common in CO₂ experiments that is the formation of ethane in relatively large amounts. It is quite possible that the slow space velocity promotes hydrogenation of ethylene and produces ethane. This reaction will be examined under the general discussion.

Catalyst number 25.

Contained copper and boron by precipitation from $\text{Cu}(\text{NO}_3)_2$ and $\text{Na}_2\text{B}_4\text{O}_7$ solution followed by thorough washing and ignition in a blast lamp. With ethanol and water the results are shown in table 6.

T A B L E 6.

Temperature °C	450
Liquid used in c.c.	45.5
Rate of flow cc/min.	0.28
Condensate c.c.	43
Gas yield in litres	1.6
Gas flow cc/min	9.7

Gas Analysis

CO_2	2.7
C_2H_4	9.8
H_2	80.0
CO	2.2
CH_4	5.5

The catalyst was reduced to the metallic state with no evidence of boron. The ignition of the borate in all probability volatilized some of the boron.

Catalyst number 27.

A mixture of Fe and Ni as chromates, prepared by precipitation from an equimolar solution of nitrates using K_2CrO_4 in slightly alkaline solution. An orange yellow precipitate was formed which was filtered, washed, dried at 110° , and crushed.

With alcohol and water the results are given in table 7.

T A B L E 7.

Temperature °C	350	400	450	500
Liquid used in c.c.	20	23	17	14
Rate of flow cc/min.	.12	.08	.07	.09
Condensate c.c.	18	18	12	-
Gas yield in litres	1.87	9.07	7.1	3.4
Gas flow cc/min.	11	27.4	27.8	21.2

Gas Analysis

CO ₂	7.3	18.5	18.9	18.9
C ₂ H ₄	1.6	2.8	3.1	4.3
H ₂	91.0	78.5	76.8	76.7
CO	nil	nil	0.7	nil
CH ₄	nil	nil	0.7	nil

The features of some of the experiments previously noted are again in evidence. Particular notice should be taken of the absence of carbon monoxide, methane and ethane in the gases.

Catalyst number 28 A

A silica supported catalyst prepared by the method of Holmes and Anderson (55) using an equimolar mixture of CrCl_3 and CuCl_2 with $\text{Na}_2(\text{SiO}_2)_x$ until neutral. This was allowed to gel and washed slightly.

With ethanol and water and the apparatus shown in fig. 2, the results are given in table 8.

T A B L E 8.

Temperature °C	350	400	450	500
Liquid used in c.c.	31.6	29.9	8.2	24.6
Rate of flow cc/min.	0.15	0.15	0.15	0.15
Condensate c.c.	25	22	7	12
Gas yield - litres	4.36	5.67	2.4	14.0
Gas flow c.c./min.	21	28	44	84

Gas Analysis

CO_2	0.5	2.7	8.6	10.2
C_2H_4	90.3	70.0	53.0	30.4
H_2	6.0	23.5	29.4	40.5
CO	0.7	0.9	0.9	0.9
CH_4	0.7	0.9	4.9	11.2
C_2H_6	1.8	2.1	3.2	6.4

A heavy mist settling as an oil was present in the exit gases. The interesting results shown above are discussed under the section on the formation of ethane.

Catalyst number 28 B.

The addition of 50% KOH to number 28 A made this catalyst. It may be considered as an alkalized Cr-Cu catalyst.

One run was made at 450° using alcohol and water, giving the results shown in Table 9.

T A B L E 9

Temperature °C	450
Liquid used in c.c.	23.7
Rate of flow cc/min.	.20
Condensate c.c.	18.0
Gas yield litres	4.2
Gas flow cc/min.	35

Gas Analysis

CO ₂	10.3
C ₂ H ₄	21.9
H ₂	61.0
CO	0.5
CH ₄	5.3
C ₂ H ₆	0.9

A yellow oil was present in the condensate. The presence of potassium has apparently favored the dehydrogenation reaction in preference to dehydration.

Catalyst number 28 C.

A portion of catalyst 28 A was allowed to stand for some time, then soaked in a solution of NiCl_2 .

The catalyst was reduced with alcohol and the results using alcohol and water are shown in table 10.

T A B L E 1 0.

Temperature °C	350	400	450
Liquid used in c.c.	86.3	49.7	25.3
Rate of flow cc/min.	.27	.25	.31
Condensate c.c.	77	42	15
Gas yield litres	7.8	7.9	7.5
Gas flow cc/min.	24	40	94

Gas Analysis.

CO_2	1.1	3.4	9.3
C_2H_4	56.8	57.7	45.0
H_2	42.1	35.2	36.2
CO	nil	nil	1.1
CH_4	nil	3.8	8.5
C_2H_6	nil	nil	nil

These results are rather unexpected showing a high ethylene production with nickel present. The nickel certainly indicated its dehydrogenating activity at lower temperatures, and the ethylene content is lower than with the first members of the series.

Catalyst number 28 D.

Another sample of the older gel of number 28 B, soaked in a solution of FeCl_3 .

The result of one run with alcohol and water is given in table 11.

T A B L E 1 1.

Temperature °C	450
Liquid used in c.c.	27.6
Rate of flow cc/min.	.25
Condensate	14.0
Gas yield in litres	10.2
Gas flow cc/min.	93

Gas Analysis.

CO_2	12.2
C_2H_4	31.1
H_2	48.3
CO	1.8
CH_4	6.1
C_2H_6	-

More oil was produced with this catalyst than with the other members of the series, probably due to the oil promoting tendencies of iron. The CO_2 is also slightly greater here than in previous runs of the series.

Catalyst number 29.

An equimolar solution of NiCl_2 , CuCl_2 and ZnCl_2 , precipitated with NaOH and dried for 12 hours at 70° , and 12 hours at 120° , and then washed thoroughly to remove excess alkali.

This catalyst was investigated rather thoroughly, using carbon dioxide and alcohol.

The first run was made at 450° with a sample reduced with hydrogen. The results are shown in table 12.

T A B L E 1 2.

Temperature $^\circ\text{C}$	450	450
Liquid used in c.c.	4.5	4
Condensate c.c.	2	1.5
CO_2 volume in litres	2.68	2.8
CO_2 flow cc/min.	50	25
Total gas yield in litres	6.26	6.64
Theoretical CO_2 percentage in gas	42.8	42.7

Gas Analysis

CO_2	52.9	40.8
C_2H_4	3.3	2.7
H_2	31.7	27.6
CO	6.3	17.8
CH_4	5.2	10.3
C_2H_6	0.6	0.9

The catalyst appeared to be carbonized. The analytical results show a definite excess of CO over CH_4 so that some source other than decomposition of acetaldehyde must be sought for the carbon monoxide. This result and those following are of interest in showing CO and H_2 to be the principal products of the reactions.

The apparent reaction of CO_2 necessitated further study and a fresh sample of the catalyst was reduced with hydrogen and alcohol. The results are shown in columns 1 - 6 of table 13. The results were not quite as expected. The carbon deposited on the catalyst was oxidized off and the catalyst reduced with hydrogen. Further tests gave the results in columns 7 and 8. The evident activity suggested another oxidation and reduction with hydrogen and alcohol. The results in columns 9 - 12 gave initial promise, but the catalyst lost its activity. The catalyst was again oxidized and again reduced with hydrogen, but apparently this rather harsh treatment had destroyed the activity of the catalyst as shown by the results in columns 13 and 14.

TABLE 13.

Column (a)	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Temperature °C	450	450	400	400	500	500	400	450	400	400	450	450	350	350
Liquid used in c.c.	4	3	10	-	7.5	8.5	4.5	5	2	6	2.5	3.8	3	6
Condensate c.c.	1	0.5	6	4	1	1	nil	trace	nil	trace	trace	trace	nil	nil
CO ₂ volume in litres	2.75	4.1	4.68	3.6	6.07	3.99	2.83	2.98	2.89	3.16	3.03	3.28	2.98	4.37
CO ₂ flow cc/min.	50	25	50	25	50	25	25	25	25	50	25	50	25	50
Total gas yield in litres	9.05	8.45	7.63	5.9	14.23	12.47	9.08	10.58	7.15	8.06	7.80	8.76	8.36	8.56
Theoretical CO ₂ percentage in gas	30.4	48.7	61.3	61.0	42.6	32.0	31.2	27.6	40.4	37.6	38.9	37.5	35.6	51.0
Gas Analysis														
CO ₂	38.5	55.4	69.2	73.2	38.7	50.2	27.8	25.8	34.9	45.7	40.7	44.4	40.2	53.7
C ₂ H ₄	4.4	3.8	2.3	1.9	4.0	3.7	0.9	2.2	1.1	1.1	nil	1.4	0.6	0.9
H ₂	31.1	30.0	23.9	17.9	45.7	33.5	25.2	38.5	22.7	32.1	19.3	24.0	25.1	27.5
CO	15.0	6.4	1.1	1.4	5.1	4.7	23.0	15.9	19.5	10.6	18.0	14.7	17.4	7.2
CH ₄	10.2	-(b)	3.6	-(b)	4.0	-(b)	21.7	17.8	21.8	10.4	-(b)	15.4	16.9	-(b)
C ₂ H ₆	0.9	-	nil	-	2.7	-	1.4	nil	nil	nil	-	nil	nil	-

(a) Columns 1 - 6 indicate catalyst reduced with hydrogen and alcohol.
 7 - 8 same sample oxidized and reduced with hydrogen.
 9 -12 again oxidized and reduced with hydrogen and alcohol.
 13 -14 oxidized and reduced with hydrogen.

(b) In some cases combustions were not made on the gas.

Another sample of catalyst 29 was reduced with hydrogen and treated with CO₂ and alcohol, as shown in columns 1 - 2 of table 14. The catalyst on removal was in good condition, but covered with a black deposit of carbon, more oily in nature than graphitic which may have come from thermal decomposition of some of the hydrocarbons as well as from CO decomposition.

The catalyst was oxidized, reduced with hydrogen, and again tested with the results shown in columns 3 and 4.

T A B L E 1 4.

Column	1	2	3	4
Temperature °C	375	425	475	500
Liquid used in c.c.	3	2	2.5	2
Condensate c.c.	nil	trace	trace	nil
CO ₂ volume in litres	3.17	2.86	2.86	2.92
CO ₂ flow cc/min.	25	25	25	25
Total gas yield in litres	6.78	6.38	7.32	7.20
Theoretical CO ₂ percentage in gas	46.8	44.8	39.1	40.5

Gas Analysis

CO ₂	47.2	53.7	38.0	45.0
C ₂ H ₄	0.4	0.7	0.4	1.1
H ₂	18.1	22.4	31.9	26.7
CO	17.2	14.2	15.0	15.8
CH ₄	17.2	-	14.5	-
C ₂ H ₆	nil	-	nil	-

Catalyst number 30.

A mixture of 10 moles of $\text{Mg}(\text{NO}_3)_2$ and 1 mole of $\text{Cr}(\text{NO}_3)_3$ was precipitated from solution by concentrated NH_4OH and this catalyst mass carefully washed and dried.

The first experiments using CO_2 and alcohol gave the results indicated in table 15.

T A B L E 1 5.

Temperature °C	450	350
Liquid used in c.c.	3	3
Condensate c.c.	2	2.5
CO_2 volume in litres	2.79	2.84
CO_2 flow cc/min	25	25
Total gas yield litres	4.82	2.90 (?)
Theoretical CO_2 percentage in gas	57.8	97

Gas Analysis

CO_2	59.6	92
C_2H_4	1.6	0.2
H_2	27.4	2.3
CO	3.2	2.6
CH_4	nil	nil
C_2H_6	8.7	3.0

The meter reading at 350° is doubtful - a small leak was discovered after the run.

At 450° a yellow mist was formed which condensed as a yellow oil, insoluble in water but soluble in 95% alcohol.

The formation of oil indicated rather interesting possibilities and the catalyst was investigated with absolute alcohol. At 300° and 350° the activity was very irregular and the gas flow unsteady. At 450° fumes were evident while at 500° the fumes were

very dense and hard to condense. The analyses of the gaseous products are given in table 16.

T A B L E 1 6.

Temperature °C	450	500
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Gas Analysis.

CO ₂	4.8	10.4
C ₂ H ₄	14.0	12.7
H ₂	80.9	71.3
CO	nil	2.6
CH ₄	nil	2.9
C ₂ H ₆	nil	nil

A yellow oil was formed in the condensate, similar to the one previously noted. A discussion of these very interesting results will be found under the section on the formation of carbon dioxide in alcohol decomposition.

Catalyst number 31.

This series of catalysts was prepared by precipitating one half of a mole of CuCl_2 with NaOH and adding $1/20$ mole of each of the following to individual samples to serve as promoters. In every case the mixture was visibly heterogeneous.

- A - cerium oxide
- B - manganese dioxide
- C - vanadium metal
- D - alumina
- E - ferric oxide
- F - titanio acid and molybdic acid
- H - bismuth metal
- J - beryllium metal

All of these catalysts were investigated using carbon dioxide and alcohol. The results are appended in table 17.

T A B L E 1 7.

	31 A	31 A	31 B	31 B	31 C	31 D	31 E	31 F	31 G	31 H	31 J
Catalyst											
Temperature °C	350	450	450	450	450	450	450	450	450	450	450
Liquid used in c.c.	3.5	2.5	9	6	1	2.5	3	3.5	5.5	4	6.5
Condensate c.c.	3	2 (b)	6	5.5	trace (c)	1	1	2	5(d)	3(e)	6
CO ₂ volume in litres	2.86	2.84	4.05	3.32	2.84	2.92	2.85	2.84	2.95	2.84	2.83
CO ₂ flow cc/min.	25	25	25	100	25	25	25	25	25	25	25
Total gas yield litres	3.08	4.82	8.50	4.08	3.84	4.86	4.98	5.02	3.37	4.43	3.40
Theoretical CO ₂ percentage in gas	92.8	58.8	47.8	81.4	73.7	60	59.2	56.5	87.5	64	83.2
Gas Analysis											
CO ₂	93.6 (a)	66.8	53.2	85.8	81.0	75.4	67.0	63.1	92.4	81.5	80.5
C ₂ H ₄		0.9	1.0	0.4	0.4	1.2	0.7	0.6	0.2	1.1	1.1
H ₂		28.7	36.1	11.0	15.5	18.8	27.8	25.6	3.2	15.1	7.2
CO		1.2	1.2	0.4	0.7	0.7	1.1	3.1	0.2	0.2	0.5
CH ₄		nil	nil	nil	nil	nil	nil	nil	1.3	-	10.7
C ₂ H ₆		2.4	8.6	2.4	2.7	3.7	3.3	7.7	2.6	-	nil

- (a) Practically no activity - slight mist initially, disappears rapidly and not reformed.
 (b) Mist formed - oily condensate.
 (c) Mist very slight, not as great as A or B
 (d) No mist - condensate light yellow
 (e) Slight mist

Catalyst number 32.

Prepared by soaking ZnO in a concentrated solution of potassium molybdate to make a paste, drying at 110°, and igniting in air with a blast lamp.

One run was made with CO₂ and alcohol, with the results shown in table 18.

T A B L E 1 8.

Temperature °C	450
Liquid used in c.c.	4
Condensate in c.c.	2
CO ₂ volume in litres	3.32
CO ₂ flow cc/min.	25
Total gas yield in litres	6.45
Theoretical CO ₂ percentage in gas	51.5

Gas Analysis

CO ₂	59.4
C ₂ H ₄	1.5
H ₂	24.1
CO	0.6
CH ₄	14.4
C ₂ H ₆	nil

This catalyst promoted the decomposition of CO and is otherwise essentially dehydrogenating.

Catalyst number 33.

This was a short series prepared by mixing solutions of $\text{Ni}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$ in varying proportions and precipitating with NaOH , after which they were washed and dried. The compositions were as follows:

- A - 25% Ni
- B - 50% Ni
- C - 75% Ni

With CO_2 and alcohol catalyst number 33 A gave the results indicated in table 19.

T A B L E 1 9.

Temperature °C	450	350	400
Liquid used in c.c.	3.5	4	3.5
Condensate in c.c.	trace	trace	trace
CO_2 volume in litres	2.84	2.84	2.5
CO_2 flow cc/min.	25	25	25
Total gas yield in litres	7.53	8.35	6.95
Theoretical CO_2 percentage in gas	37.7	34.0	37.1

Gas Analysis

CO_2	53	45.2	47.2
C_2H_4	nil	nil	nil
H_2	16.0	5.9	10.5
CO	3.6	3.2	3.7
CH_4	27.3	45.7	38.8
C_2H_6	nil	nil	nil

The large methane production compared to CO and hydrogen is unusual. The action of methane and CO_2 on the same catalyst was examined. CH_4 and CO_2 were mixed in equal volumes and passed over the catalyst at 450° at a rate of 70 cc/min. There was an 8% expansion in gas volume and the exit gas contained 2.8% CO

and 4.5% H₂ while the catalyst appeared carbonized. The reaction was quite probably



but this was not investigated further.

Catalyst 33 B was investigated with alcohol and water, with the results given in table 20. Runs at 200° and 250° gave no indication of reaction.

T A B L E 2 0.

Temperature °C	275	300	325	350
Liquid used in c.c.	42.4	45.6	47.8	54
Rate of flow cc/min.	.34	.83	.68	.83
Condensate c.c.	40	40	44	50
Gas yield in litres	2.1	2.1	2.8	1.8
Gas flow cc/min.	18.4	38.2	40	27.7

Gas Analysis

CO ₂	7.2	1.8	2.7	1.9
C ₂ H ₄	1.7	1.4	1.1	1.9
H ₂	79.2	76.7	80.2	85.6
CO	2.7	4.3	5.3	4.0
CH ₄	7.4	11.5	10.7	6.5
C ₂ H ₆	1.8	4.1	nil	nil

Catalyst number 33 C was studied with all three reaction mixtures. With CO₂ and alcohol, two runs were made, as noted in columns 1 and 2, table 21. The catalyst was oxidized and reduced again, and the results are shown in columns 3 and 4.

T A B L E 2 1.

Column	1	2	3	4
Temperature °C	450	350	300	275
Liquid used in c.c.	4	4	5	4.5
Condensate c.c.	trace	trace	trace	trace
CO ₂ volume in litres	2.86	2.89	2.86	2.84
CO ₂ flow cc/min.	25	25	25	25
Total gas yield in litres	8.05	7.23	9.42	7.20
Theoretical CO ₂ percentage in gas	35.6	40	30.4	39.4

Gas Analysis

CO ₂	54.9	50.8	34.7	48.1
C ₂ H ₄	nil	nil	nil	nil
H ₂	17.9	12.6	29.0	27.8
CO	2.9	1.8	14.1	7.6
CH ₄	13.7	34.8	15.9	16.5
C ₂ H ₆	10.7	nil	6.3	nil

The vigorous treatment apparently did not deactivate the catalyst. The decomposition of CO at 350-450° is evident, but not as noticeable at the lower temperatures agreeing with other results.

The results with ethanol and water are given in table 22. After the second run the catalyst was badly carbonized and the results in the third column were obtained after the catalyst had been oxidized and reduced.

T A B L E 2 2.

Temperature °C	300	500	275
Liquid used in c.c.	35.2	26.2	33.3
Rate of flow cc/min.	.35	.33	.37
Condensate c.c.	28	4	27
Gas yield in litres	6.2	28.7	4.1
Gas flow cc/min.	62	360	45

Gas Analysis.

CO ₂	3.0	20.4	2.5
C ₂ H ₄	0.4	nil	0.2
H ₂	65.0	44.6	56.5
CO	10.0	6.8	15.3
CH ₄	15.0	22.2	23.6
C ₂ H ₆	6.7	5.9	1.9

It will be noted that the activity after oxidation and reduction is much the same with a decrease in the ethane content and corresponding increase in methane.

Using pure alcohol, the results are indicated in table 23. After the first run the catalyst was slightly carbonized and the results in the last two columns were obtained after the catalyst had been oxidized and reduced.

T A B L E 2 3.

Temperature °C	300	450	375
Liquid used in c.c.	23.2	14.1	21.1
Rate of flow cc/min.	.23	.31	.24
Condensate c.c.	11	4	12
Gas yield in litres	10.7	11.3	13.5
Gas flow cc/min.	107	250	160

Table 23 - continued.

Gas Analysis.

CO ₂	4.2	4.9	3.2
C ₂ H ₄	1.2	3.4	3.2
H ₂	59.8	53.0	50.7
CO	10.4	11.9	15.0
CH ₄	13.1	11.7	14.1
C ₂ H ₆	11.2	17.1	13.6

These results are not very different from those with alcohol and water, except in the ethane content. This will be further discussed under ethane formation.

Catalyst number 34.

An equimolar mixture of CoCl_2 and $\text{Zn}(\text{NO}_3)_2$ precipitated with NaOH , washed thoroughly and dried.

Using ethanol and water the results obtained in two runs are those in table 24.

T A B L E 2 4.

Temperature °C	325	450
Liquid used in c.c.	41.4	43.4
Rate of flow cc/min.	.64	.72
Condensate c.c.	40	30
Gas yield in litres	2.2	13.2
Gas flow cc/min.	34	220

Gas Analysis

CO_2	5.4	6.9
C_2H_4	0.2	1.0
H_2	85.6	76.5
CO	1.5	1.5
CH_4	7.3	23.9
C_2H_6	nil	nil

At 450° the increase in methane and decrease in H_2 indicates hydrogenation of CO or CO_2 .

Catalyst number 35.

This set of catalysts was prepared by dissolving TeO_2 in hot NaOH and then added to the solutions of

A - $\text{Zn}(\text{NO}_3)_2$ precipitating ZnTeO_3
 B - $\text{Ni}(\text{NO}_3)_2$ precipitating NiTeO_3
 C - $\text{Cr}(\text{NO}_3)_2$ precipitating $\text{Cr}_2(\text{TeO}_3)_3$

The precipitates were carefully washed and dried.

The results with alcohol and water are shown in table 25.

At 300° there was no reaction,*but the condensate had a very pungent odor.

T A B L E 2 5.

Catalyst	35 A	35 B	35 C
Temperature $^\circ\text{C}$	450	500	450
Liquid used in c.c.	39.2	46.7	52.1
Rate of flow cc/min.	0.78	0.78	0.55
Condensate c.c.	34	44	50
Gas yield in litres	2.1	2.0	3.5
Gas flow cc/min.	42	33	37

Gas Analysis

CO_2	3.8	2.3	2.8
C_2H_4	5.8	1.7	22.0
H_2	90.0	84.3	67.7
CO	0.4	2.6	0.6
CH_4	nil	9.0	6.9
C_2H_6	nil	nil	nil

The primary metal is evidently the controlling factor in the activity of these catalysts.

Catalyst number 36.

A solution of CrCl_3 was precipitated with NH_4OH and washed and to one mole of this hydroxide one tenth of a mole of one of the following was added:

A - Titanic acid H_2TiO_3
 B - PbO
 C - Molybdic acid H_2MoO_4

The results with alcohol and water are appended in table 26. None of the catalysts were active at 350° , although, here again, the condensates had a very peculiar odor which was not alcoholic.

T A B L E 2 6.

Catalyst	36 A	36 B	36 C
Temperature $^\circ\text{C}$	450	450	450
Liquid used in c.c.	32.8	34.5	33.3
Rate of flow cc/min.	0.55	0.53	0.60
Condensate c.c.	30	22	30
Gas yield in litres	1.4	7.4	1.5
Gas flow cc/min.	23	114	27

Gas Analysis.

CO_2	2.3	9.7	5.8
C_2H_4	38.5	17.9	21.0
H_2	49.7	8.2	69.0
CO	nil	0.2	nil
CH_4	3.0	nil	nil
C_2H_6	6.5	64.3	4.3

The promoter is certainly the most active constituent in these catalysts favoring respectively dehydration, hydrogenation and dehydrogenation.

Catalyst number 37.

Precipitated ZnCrO_4 from $\text{Zn}(\text{NO}_3)_2$ and K_2CrO_4

The results with alcohol and water are given in table 27.

T A B L E 2 7

Temperature °C	350	450
Liquid used in c.c.	15.2	44.8
Rate of flow cc/min.	0.33	0.6
Condensate c.c.	14	38
Gas yield in litres	0.6	4.6
Gas flow cc/min.	13	61

Gas Analysis

CO_2	5.6	17.3
C_2H_4	6.7	2.4
H_2	76.3	77.7
CO	3.3	1.3
CH_4	8.1	1.1
C_2H_6	nil	nil

The absence of CH_4 and increase of CO_2 at 450° indicates that the aldehyde is not being decomposed into CO and CH_4 , but is undergoing a more complex reaction.

Catalyst number 38.

Precipitated NiCrO_4 using a solution of $\text{Ni}(\text{NO}_3)_2$ and K_2CrO_4 .

The results with carbon dioxide and water are indicated in table 28.

T A B L E 2 8.

Temperature °C	450	350	350
Liquid used in c.c.	4	4	5
Condensate c.c.	nil	trace	trace
CO ₂ volume in litres	2.84	2.86	2.86
CO ₂ flow cc/min.	25	50	25
Total gas yield in litres	6.52	7.35	7.43
Theoretical CO ₂ percentage in gas	41.9	38.9	38.5

Gas Analysis

CO ₂	43.9	53.0	48.0
C ₂ H ₄	nil	0.4	0.4
H ₂	14.8	8.3	4.0
CO	4.0	1.5	1.5
CH ₄	37.4	36.8	46.1
C ₂ H ₆	nil	nil	nil

The results using alcohol and water will be considered separately under the discussion of nickel-chromium catalysts.

Catalyst number 39.

Precipitated CdCrO_4 from a solution of $\text{Cd}(\text{NO}_3)_2$ using K_2CrO_4 .

The results from CO_2 and alcohol are given in table 29.

T A B L E 2 9.

Temperature °C	350	450
Liquid used in c.c.	5	5
Condensate c.c.	4.5	3.5
CO_2 volume in litres	2.84	3.0
CO_2 flow cc/min.	25	25
Total gas yield in litres	3.04	5.27
Theoretical CO_2 percentage in gas	93.4	57.0

Gas Analysis

CO_2	84.0	51.5
C_2H_4	1.2	2.9
H_2	14.8	44.6
CO	nil	1.0
CH_4	nil	nil

Catalyst number 40.

CuCrO_4 precipitated from a solution of $\text{Cu}(\text{NO}_3)_2$ using K_2CrO_4 .

Using water and alcohol, the results are shown in table 30.

T A B L E 3 0.

Temperature °C	350	450
Liquid used in c.c.	49.5	51
Rate of flow cc/min.	6.6	5.1
Condensate c.c.	-	44
Gas yield in litres	0.8	1.6
Gas flow cc/min.	10	16

Gas Analysis.

CO_2	4.8	9.7
C_2H_4	nil	4.7
H_2	86.6	80.8
CO	nil	nil
CH_4	8.5	4.8

The CH_4 was, in all probability, formed by the hydrogenation of CO_2 .

Catalyst number 41.

A mixture of 5 moles of ZnO and 1 mole of MoO_3 suspended in water and evaporated to dryness, using a motor stirrer to keep the constituents thoroughly mixed.

The results with alcohol and water, in which the needle valve vaporizer was employed to regulate space velocities, are shown in table 31.

T A B L E 3 1.

Temperature °C	350	350	450	450
Liquid used in c.c.	47.6	41.5	12	25
Rate of flow cc/min.	0.95	0.49	0.22	0.63
Condensate c.c.	45.0	40.0	3	21
Gas yield in litres	1.7	1.4	3.4	2.86
Gas flow cc/min.	34	16	62	70

Gas Analysis.

CO_2	2.8	1.5	21.4	9.3
C_2H_4	9.0	12.7	9.6	10.8
H_2	64.9	56.3	58.6	69.5
CO	3.0	nil	0.2	0.2
CH_4	20.3	29.5	10.3	10.2
C_2H_6	nil	nil	nil	nil

Evidently this is a mixed catalyst favoring hydrogenation of CO and CO_2 .

With carbon dioxide and alcohol the results are indicated in table 32.

T A B L E 3 2.

Temperature °C	350	450
Liquid used in c.c.	5.5	4
Condensate c.c.	3.5	nil
CO ₂ volume in litres	3.96	2.64
CO ₂ flow cc/min.	30	30
Total gas yield in litres	5.36	5.87
Theoretical CO ₂ percentage in gas	74	44.9

Gas Analysis

CO ₂	62.2	40.2
C ₂ H ₄	3.1	9.3
H ₂	16.1	24.9
CE	nil	3.3
CH ₄	13.2	-
C ₂ H ₆	5.5	-

Catalyst number 42.

A mixture of 5 moles of ZnO and 1 mole of Al_2O_3 suspended in water and evaporated as with 41.

The results using CO_2 and alcohol are indicated in table 33.

T A B L E 3 3.

Temperature °C	350	450
Liquid used in c.c.	4	6
Condensate c.c.	3.8	?
CO_2 volume in litres	4.22	3.96
CO_2 flow cc/min.	25	25
Total gas yield in litres	4.85	8.70
Theoretical CO_2 percentage in gas	82.0	45.5

Gas Analysis.

CO_2	76.2	48.0
C_2H_4	4.0	8.9
H_2	17.5	39.3
CO	nil	nil
CH_4	-	1.3
C_2H_6	-	1.3

Catalyst number 43.

Prepared by precipitating a solution containing 5 moles of ZnCl_2 and 1 mole of CrCl_3 using NH_4OH , following which the catalyst was washed thoroughly and dried.

The results obtained from alcohol and water are given in table 34.

T A B L E 3 4.

Temperature °C	450	350
Liquid used in c.c.	42.8	51
Rate of flow cc/min.	.66	.68
Condensate c.c.	38	45
Gas yield in litres	6.8	1.14
Gas flow cc/min.	104	15

Gas analysis

CO_2	12.9	5.3
C_2H_4	6.4	4.0
H_2	79.6	88.6
CO	nil	nil
CH_4	1.1	2.1

Catalyst number 44.

This was one of the catalysts used by Audibert and Raineau (122) prepared as follows: Precipitate $\text{Fe}(\text{NO}_3)_3$ with hot Na_2CO_3 and add H_3PO_4 . Add an equimolar solution of $\text{Mn}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ and precipitate with hot Na_2CO_3 , wash, filter and add K_2CO_3 in a minimum amount of solution. The quantities are adjusted to give the following ratio; 0.02 Fe, 0.02 K, 0.3 P, 1.0 Cu, 1.0 Mn.

With alcohol and water, the results are shown in table 35.

T A B L E 3 5.

Temperature °C	350	450
Liquid used in c.c.	51	57.7
Rate of flow cc/min.	0.60	0.58
Condensate c.c.	41	45
Gas yield in litres	7.50	12.8
Gas flow cc/min.	88	128

Gas Analysis.

CO_2	7.3	18.1
C_2H_4	1.4	2.5
H_2	83.3	77.7
CO	nil	nil
CH_4	8.0	1.6

Catalyst number 45.

Prepared in a similar manner to number 44, with the substitution of H_3BO_3 for H_3PO_4 . The rations were adjusted to the following; 0.02 Fe, 0.02 K, 0.15 B, 1.0 Cu, 1.0 Mn.

The results with alcohol and water are tabulated in table 36.

T A B L E 3 6.

Temperature °C	350	450
Liquid used in c.c.	26.1	28.1
Rate of flow cc/min.	0.65	0.56
Condensate c.c.	22	21
Gas yield in litres	5.05	8.60
Gas flow cc/min.	126	170

Gas Analysis.

CO_2	6.8	18.4
C_2H_4	3.0	3.0
H_2	88.1	78.7
CO	0.2	nil
CH_4	1.9	nil

The results with catalyst number 46 will be discussed under the nickel-chromium series of catalysts.

Catalyst number 47.

Prepared by boiling Enduro KA 2 Nirosta Steel turnings in 50% KOH for several hours. The approximate composition of this steel as given by The Central Alloy Steel Corporation is C less 0.16%, Mn less than 0.50%, P less than 0.025%, S less than 0.025%, Si less than 0.050%, Cr 17-20%, Ni 7-10%.

This catalyst was apparently inactive at 350-450° with alcohol and water solution passing over unchanged and no gas being formed.

Catalyst number 48.

Enduro steel turnings were broken up and used in this state.

This catalyst was also entirely inactive, and was not investigated further.

The Reactions of Nickel-chromium catalysts.

The results with the catalysts containing nickel and chromium prepared in various ways proved particularly interesting and were investigated in much greater detail than any of the other catalysts. A short review of the activities of these individual components seems to be in order at this stage.

The dehydrogenating action of nickel is well known and its action upon ethyl alcohol has been reported frequently. Sabatier and Senderens (24) found that reduced nickel acted violently to produce hydrogen and acetaldehyde, and at temperatures around 180° the aldehyde was decomposed into methane and carbon monoxide, while at 230° this latter was further decomposed to carbon and CO_2 . Adkins and Lazier (36) found a variation in the activity of nickel depending upon the reducing agent although it was essentially dehydrogenating in all cases.

As mentioned in the first part of this thesis, chromium is a mixed catalyst promoting both dehydration and dehydrogenation simultaneously, but the ratio of these reactions varies considerably with the method of preparation. The blue precipitated hydroxide produces 91% ethylone, but after calcination produces only 40% C_2H_4 , and the oxide prepared by the ignition of ammonium bichromate yields gaseous products containing only 38% C_2H_4 , according to Lamoine (28).

Catalyst number 38.

Prepared as previously described by the precipitation of nickel chromate.

The first runs with alcohol and water were made with the catalyst used previously on CO₂ and alcohol and it was slightly carbonized. The results with this catalyst are indicated in table 37.

T A B L E 3 7.

Temperature °C	300	350	400
Liquid flow cc/min.	0.55	0.55	0.55
Ratio Liquid in Liquid out	1.1	1.3	-
Gas flow cc/min.	100	300	420

Gas Analysis.

CO ₂	7.4	7.5	18.2
C ₂ H ₄	1.3	0.8	0.2
H ₂	46.0	49.5	40.5
CO	21.7	20.2	6.2
CH ₄	23.4	22.0	25.0

A fresh sample of this catalyst gave the results shown in table 38. It will be noticed that on this more active catalyst the ethylene production is down while the carbon dioxide is up, at the expense of the CO. The relatively lower hydrogen content also served to indicate hydrogenation of the carbon oxides.

T A B L E 3 8.

Temperature °C	350	450
Liquid flow cc/min.	0.55	0.55
Ratio <u>Liquid in</u> <u>Liquid out</u>	3.5	4.4
Gas flow cc/min.	420	280

Gas Analysis.

CO ₂	23.8	23.2
C ₂ H ₄	nil	0.8
H ₂	34.2	32.7
CO	3.7	1.1
CH ₄	38.3	42.2

In an effort to evaluate the effect of water in the alcohol a run was made with a fresh sample of the catalyst using 66 molecular percent water and 34% alcohol. The results appended in table 39 are very similar to those given above, which suggests that water is not entering into the reaction.

T A B L E 3 9.

Temperature °C	300	350	400
Liquid flow cc/min.	0.65	0.65	0.65
Ratio <u>Liquid in</u> <u>Liquid out</u>	-	-	1.8
Gas flow cc/min.	350	400	550

Gas Analysis.

CO ₂	17.8	20.5	19.9
C ₂ H ₄	0.7	0.4	1.1
H ₂	36.9	27.8	40.5
CO	7.4	5.4	6.9
CH ₄	37.2	47.9	31.8

This sample of catalyst was then oxidized and reduced and rerun using equimolar alcohol and water at 350°. The ratio

of liquids was 1.8 with a flow of 0.65 cc/min., while gases were produced at 80cc/min. having the following composition:

CO ₂	14.2
C ₂ H ₄	0.2
H ₂	51.9
CO	11.3
CH ₄	22.2

It will be noted that while the effectiveness of the nickel relative to the chromium has not been impaired, the hydrogenating activity of the nickel has been reduced as evidenced by the relatively higher hydrogen and CO percentage and the low methane content.

This catalyst was then oxidized and reduced with hydrogen for 15 hours to find the effect of prolonged reduction. The results are indicated in table 40.

T A B L E 4 0.

Temperature °C	350	400
Liquid flow cc/min.	0.65	0.65
Ratio Liquid in Liquid out	-	3.2
Gas flow cc/min.	50	270

Gas Analysis.

CO ₂	3.4	7.1
C ₂ H ₄	2.0	0.7
H ₂	61.6	47.5
CO	18.0	19.3
CH ₄	14.9	25.4

This catalyst was not very active and evidently prolonged reduction has no beneficial effects. It was not active below 350° and even at that temperature its hydrogenating activity

is noticeably weak.

Another sample of this catalyst was reduced with carbon monoxide, the reaction being carefully controlled to prevent carbon formation on the catalyst. This catalyst was inactive at low temperatures, but at 500°, with a liquid ratio of 4, it produced gas at the rate of 350 cc/min. with the following composition:

CO ₂	18.2
C ₂ H ₄	0.2
H ₂	40.5
CO	6.2
CH ₄	35.0

To further investigate the influence of reducing agents another sample of this catalyst was reduced at 285° with alcohol, care being taken to prevent carbon deposition. The results with this catalyst are shown in table 41. It will be noticed that in this case alcohol reduction is not as satisfactory as hydrogen reduction, and the catalyst is not as active. No carbon was deposited on the catalyst until the temperature was above 350°.

T A B L E 4 1

Temperature °C	300	350	375	400	425
Liquid flow cc/min.	0.5	0.5	0.5	0.5	0.5
Ratio <u>Liquid in</u>					
<u>Liquid out</u>	1.05	1.1	1.4	5.0	5.2
Gas flow cc/min.	25	50	120	250	200

Table 41 - continued.

Gas Analysis.

CO ₂	5.9	3.3	3.8	23.3	23.2
C ₂ H ₄	2.8	1.6	1.6	0.5	0.4
H ₂	62.6	66.0	45.5	27.4	28.4
CO	11.4	15.2	23.9	4.1	3.8
CH ₄	17.3	13.9	25.2	34.9	44.2

The temperature at which carbon deposition occurs corresponds approximately with the abrupt change in the nature of the gas between 375 and 400°C. Just as with the other results reported on this catalyst the secondary reactions are evidently decomposition and hydrogenation of the oxides of carbon.

In view of the relatively large quantities of carbon formed in many cases, it was deemed necessary to investigate the possible activity of such carbon. A blank run using activated charcoal in place of catalyst, however, gave negative results and it was concluded that the carbon would not influence the catalytic decomposition.

Catalyst number 46.

This was prepared by tritulating with water an equimolar mixture of nickelous oxide and chromic oxide. When thoroughly mixed the catalyst was dried at 110°.

It was not expected that this would be a very active catalyst in view of the results obtained with other catalysts similarly prepared. This proved to be the case with a temperature of 350° the initial gas yield was 200 cc/min. but rapidly dropped to a few cc/min. the results of two runs are appended in table 42.

T A B L E 4 2.

Temperature °C	350	450
Liquid flow cc/min.	0.75	0.75
Ratio Liquid in Liquid out	1.2	1.2
Gas flow cc/min.	slight	55

Gas Analysis.

CO ₂	6.9	8.1
C ₂ H ₄	2.4	3.6
H ₂	78.7	72.9
CO	3.5	4.1
CH ₄	8.5	11.4

Here is the first indication of an appreciable dehydrating action of chromium, but the yields are still not what might be expected, even though this was an inactive form of chromium.

Adkins has repeatedly stressed the importance of catalyst structure, and the reducing agent in catalytic activity, and in

view of the method of preparation of this sample it was decided to investigate the effect of reducing with alcohol. The results are indicated in table 43, and the increased activity is evident at once. The activity is markedly different as reported by Adkins and Lazier (36), but the total yields of gaseous products are much greater.

T A B L E 4 3.

Temperature °C	350	450
Liquid flow cc/min.	0.75	0.75
Ratio Liquid in Liquid out	1.3	1.9
Gas flow cc/min.	150	300

Gas Analysis.

CO ₂	0.4	9.3
C ₂ H ₄	1.1	2.0
H ₂	62.0	45.7
CO	18.9	19.4
CH ₄	17.6	23.7

The ratio of ethylene in these results indicates that the activating action of the alcohol was largely evident on the nickel and not on the chromium.

Catalyst number 49.

Prepared by precipitating together hydroxides of nickel and chromium from an equimolar solution of the nitrates using NaOH. The washed precipitate was dried at 110°, pulverized, triturerated with water and dried again at 110°.

The results with this catalyst using alcohol and water are given in table 44.

T A B L E 4 4.

Temperature °C	230	300	350	400	425
Liquid flow cc/min.	0.75	0.75	0.75	0.75	0.75
Ratio <u>Liquid in</u>					
<u>Liquid out</u>	1.2	1.6	1.6	2.2	
Gas flow cc/min.	200	320	420	600	400

Gas Analysis.

CO ₂	5.2	11.3	16.8	15.5	16.4
C ₂ H ₄	0.9	1.5	4.0	2.9	2.0
H ₂	54.1	44.4	43.0	45.0	56.8
CO	16.0	19.4	11.9	12.2	6.1
CH ₄	23.9	23.3	25.9	25.1	18.3

It will be noticed here that there seems to be a definite point of inflection of catalytic activity in which hydrogen and CO reach a minimum and CH₄ and CO₂ a maximum. This feature will be noticed with most of the catalysts in this series. The increase in ethylene content of the gases indicates considerable enhancement of the activity of chromium by this method of preparation. The catalyst lost some of its activity at 425°, as evidenced by the decreased gas flow and increased hydrogen content. A second run at 230° produced only 70 c.c. of gas per minute, with a com-

position identical with that of the first run at this temperature. This reduction in activity may be due to a decrease in active catalytic surface by carbon deposition, since there was no carbon present on the catalyst in the first run, but was formed subsequently during the experiments at higher temperatures.

The next series of catalysts were prepared from nickel and chromium hydroxides precipitated from a solution of the nitrate using NaOH. The washed hydroxides were mixed wet in various proportions, dried at 110° and analysed for percentage composition. The series contained the following percentages of nickelic oxide: 97, 86, 80, 66, 50, 40 and 9.

Catalyst number 56. -

contained 97% nickelic oxide. The results with alcohol and water are given in table 45. Two runs were made, as indicated in the table, and certain features should be noted. As the temperature was raised the activity of the catalyst, as measured by gas flow, reached a maximum, and at about the same temperature the nature of the decomposition seemed to change.

T A B L E 4 5.

First run.

Temperature °C	235	265	300	325	350
Liquid flow cc/min.	0.75	0.75	0.75	0.75	0.75
Ratio <u>Liquid in</u> <u>Liquid out</u>	-	-	-	-	2.4
Gas flow cc/min.	400	425	600	500	450

Gas Analysis

CO ₂	16.6	23.5	24.4	24.3	23.1
C ₂ H ₄	0.7	0.8	0.4	0.6	0.6
H ₂	39.0	25.4	17.8	29.0	30.9
CO	9.9	2.3	0.6	2.4	2.2
CH ₄	33.9	48.1	57.0	43.8	43.1

Second run.

Temperature °C	260	300	350	400	450
Liquid flow cc/min.	0.75	0.75	0.75	0.75	0.75
Ratio Liquid in Liquid out	-	-	-	-	3.9
Gas flow cc/min.	425	600	700	525	500

Gas Analysis

CO ₂	15.9	23.7	22.1	21.5	15.4
C ₂ H ₄	0.2	0.8	0.6	0.2	0.8
H ₂	37.8	32.2	29.9	44.8	50.3
CO	11.8	3.0	2.9	3.4	13.0
CH ₄	34.4	42.1	44.6	33.9	21.7

The nature of these results will be more clearly indicated by the graphs given in figures 9 and 10. Carbon was deposited on the catalyst at all temperatures, but there is an excess of carbon dioxide over that expected from the amount of methane present. It will also be noted that the dehydrating power of chromium has been almost completely suppressed with so much nickel present. The protective action of water when used with copper catalysts (47a) is not in evidence in this case.

FIGURE 9

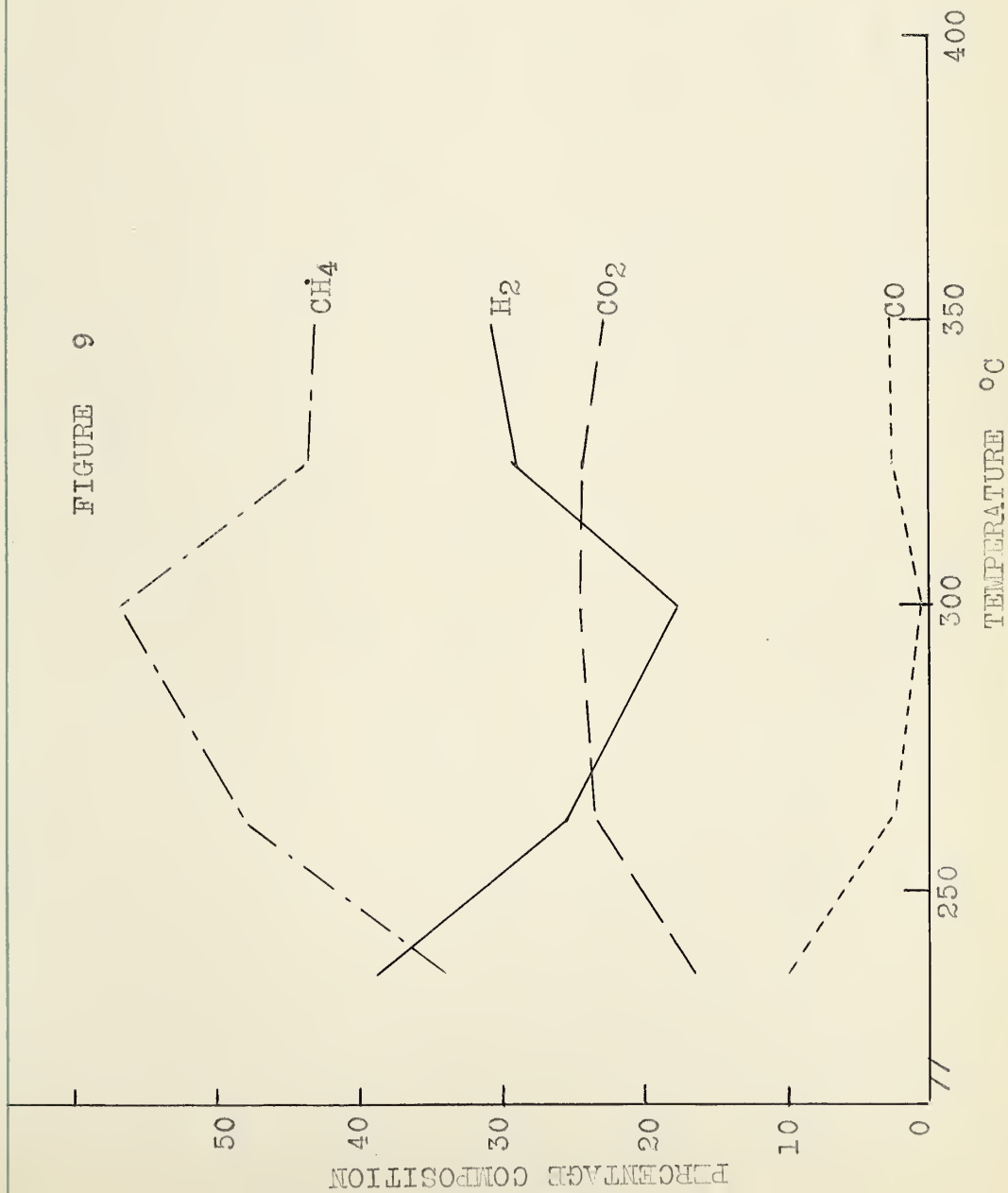
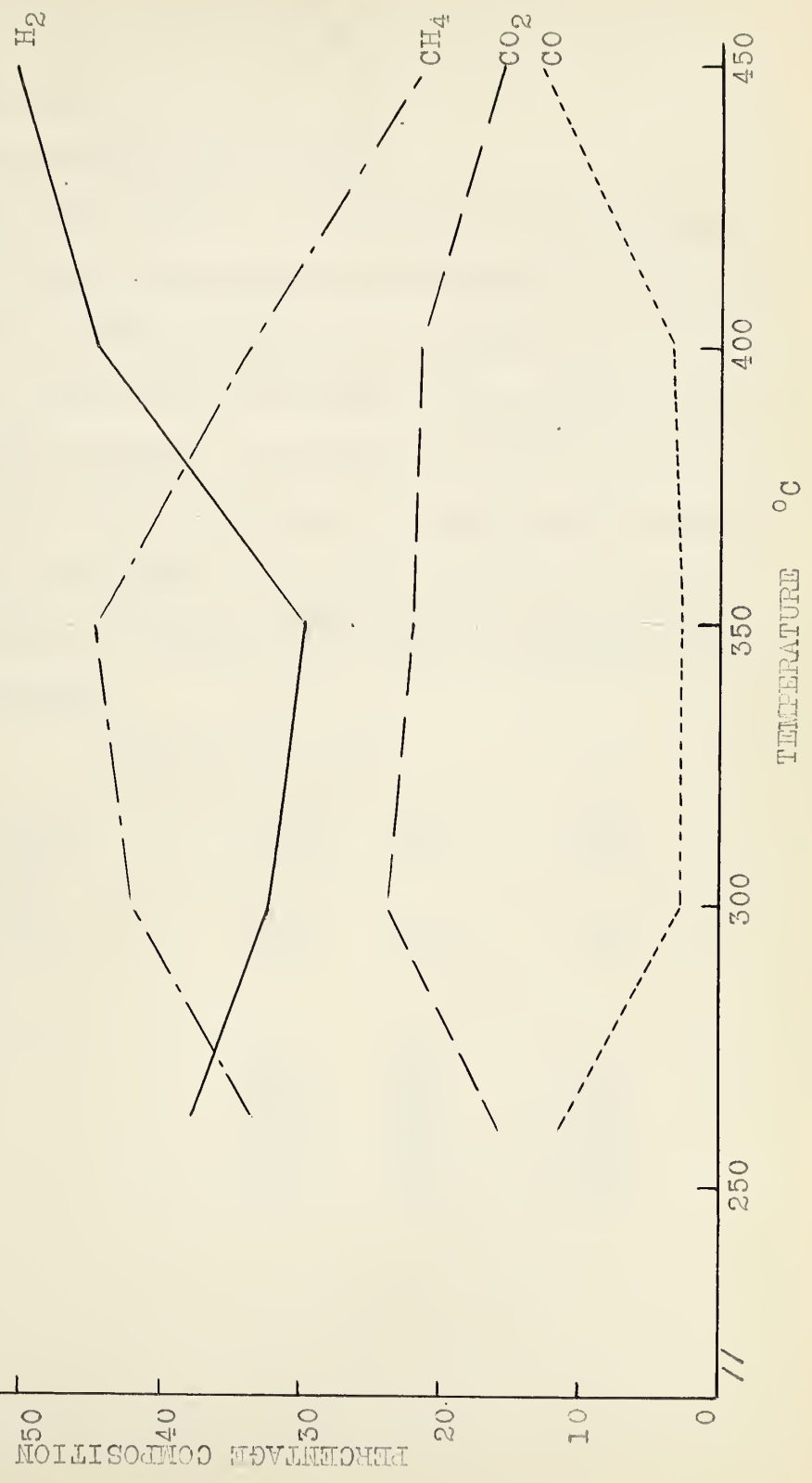


FIGURE 10



Catalyst number 52

contained 86% nickelic oxide.

The results with this catalyst on its first run were exactly like those in the second run with catalyst 56. There was a large amount of carbon deposited on the catalyst and this was burned off in a stream of oxygen at 300°. It was again reduced and its activity examined. As indicated in table 46 this treatment altered the nature of the catalyst greatly, while the hydrogen and methane are present in the same ratio, the CO reached a maximum instead of a minimum, and the CO₂ is a minimum at the changing temperature.

T A B L E 4 6.

Temperature °C	450	410	350
Liquid flow cc/min.	0.75	0.75	0.75
Ratio <u>Liquid in</u>			
<u>Liquid out</u>	-	-	-
Gas flow cc/ min.	450	300	150

Gas Analysis.

CO ₂	17.1	15.7	15.4
C ₂ H ₄	nil	0.7	1.5
H ₂	58.5	44.4	58.8
CO	8.3	12.1	9.1
CH ₄	16.3	27.1	15.1

Catalyst number 52

contained 80% nickelic oxide.

The results here were very similar to those of catalyst number 56, and are indicated in table 47.

T A B L E 4 7

Temperature °C	240	300	350	450	500
Liquid flow cc/min.	0.75	0.75	0.75	0.75	0.75
Ratio <u>Liquid in</u> <u>Liquid out</u>	-	1.5	-	-	4.8
Gas flow cc/min.	220	600	800	800	800

Gas Analysis

CO ₂	8.3	16.4	22.0	20.4	16.0
C ₂ H ₄	1.4	0.5	0.5	0.4	0.4
H ₂	40.8	39.4	31.8	40.4	49.3
CO	19.5	11.3	4.7	6.8	10.4
CH ₄	30.2	32.4	40.9	32.1	23.9

These results are more clearly shown in figure 11, and for comparative purposes they are plotted with those obtained in the second run with catalyst 56, in figure 12.

FIGURE 11

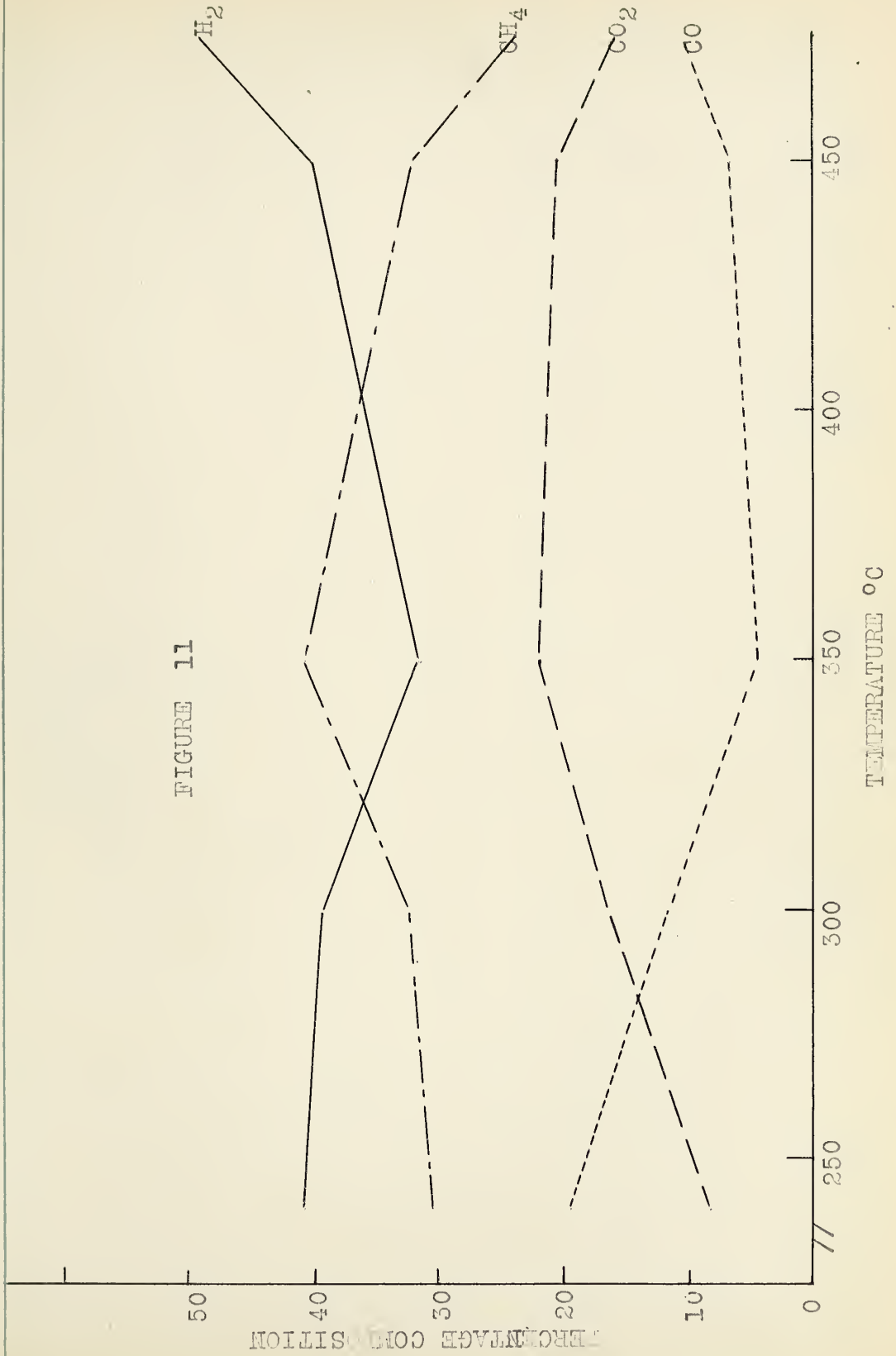
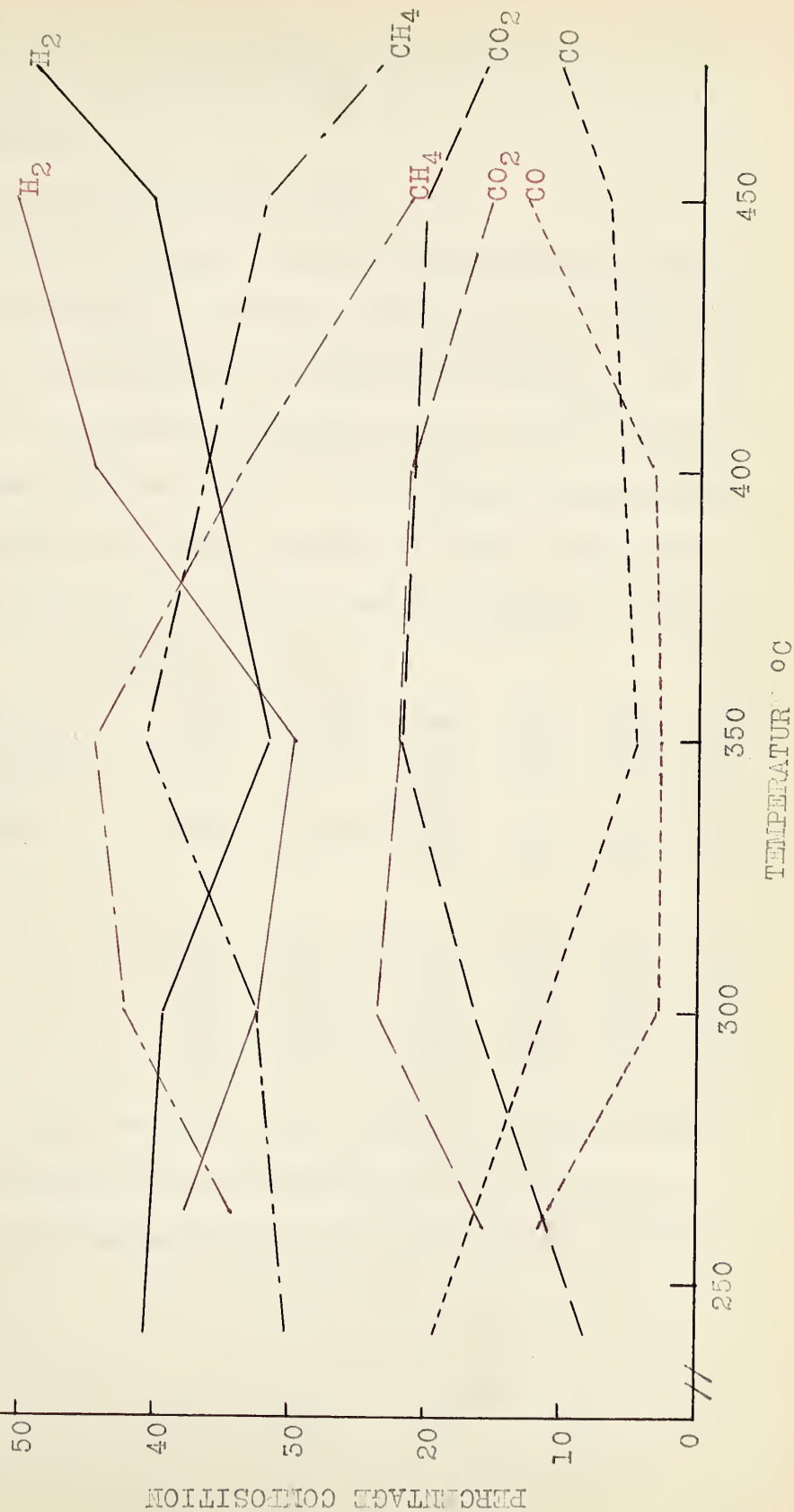


FIGURE 12

Catalyst 52

Catalyst 56(second run)



Catalyst number 53.

contained 66% nickelic oxide.

The results with this catalyst and with the preceding one indicate that the increase in chromium content changed the temperature of inversion, increasing with an increase in chromium. This is probably due to the decrease in surface area of nickel exposed which would need a higher degree of activation to accomplish the results attainable with larger surface at a lower temperature.

The experimental results with this catalyst are given in table 48.

T A B L E 4 8.

Temperature °C	235	250	300	350	400	460
Liquid flow cc/min.	0.75	0.75	0.75	0.75	0.75	0.75
Ratio <u>Liquid in</u>						
Liquid out	-	-	3.6	-	-	4.8
Gas flow cc/min.	350	500	525	550	600	600

Gas Analysis.

CO ₂	17.6	21.6	24.1	25.5	22.0	19.5
C ₂ H ₄	1.1	0.9	0.4	0.8	0.4	0.6
H ₂	30.6	26.8	19.4	12.6	29.2	41.5
CO	8.3	3.9	1.1	0.8	2.9	6.5
CH ₄	42.5	46.8	55.3	60.3	44.7	32.0

The general nature of these results is shown in Figure

13. The methane and hydrogen production on this catalyst is compared with the same quantities in the first run on catalyst 56.

FIGURE 13

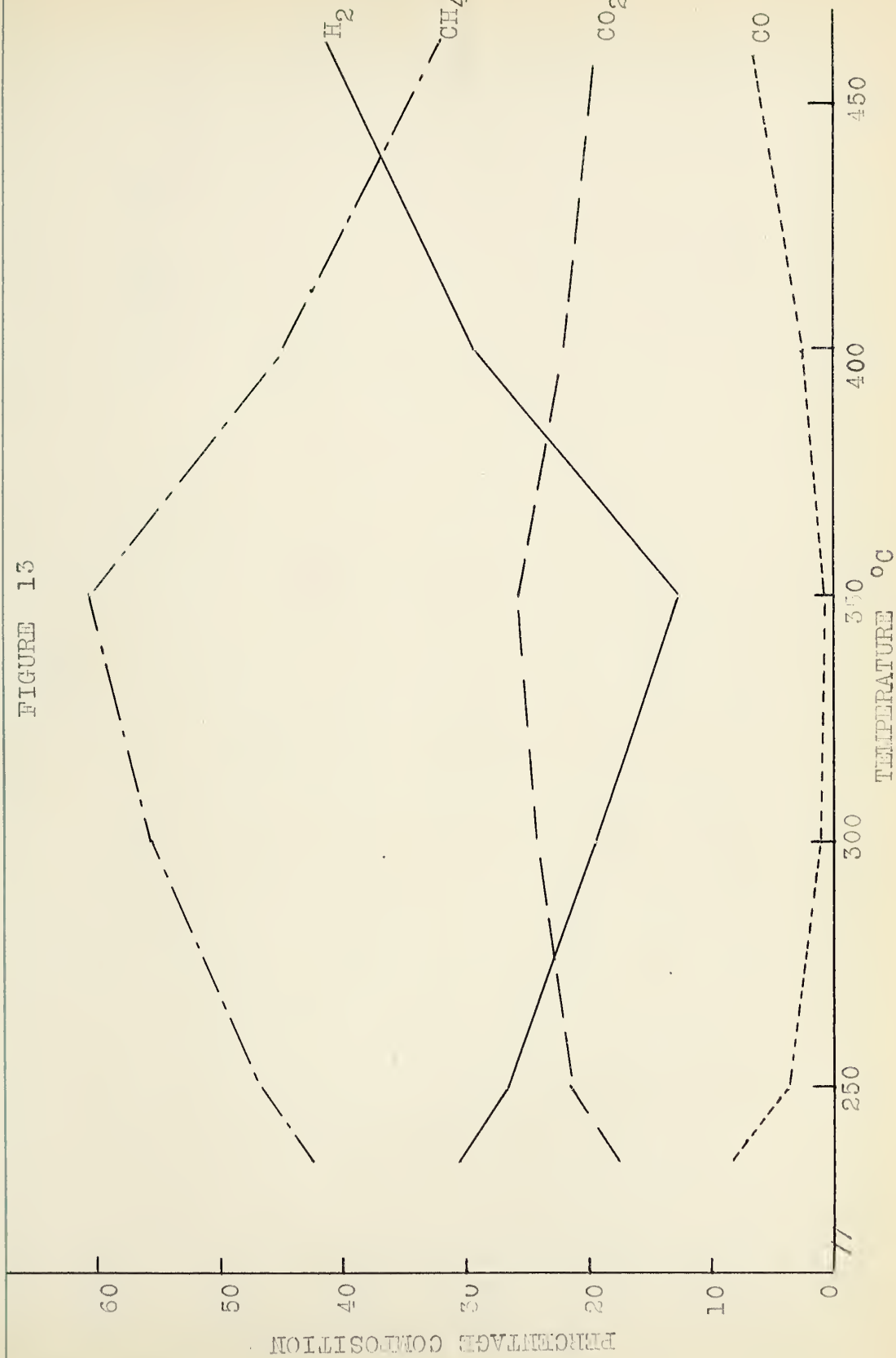
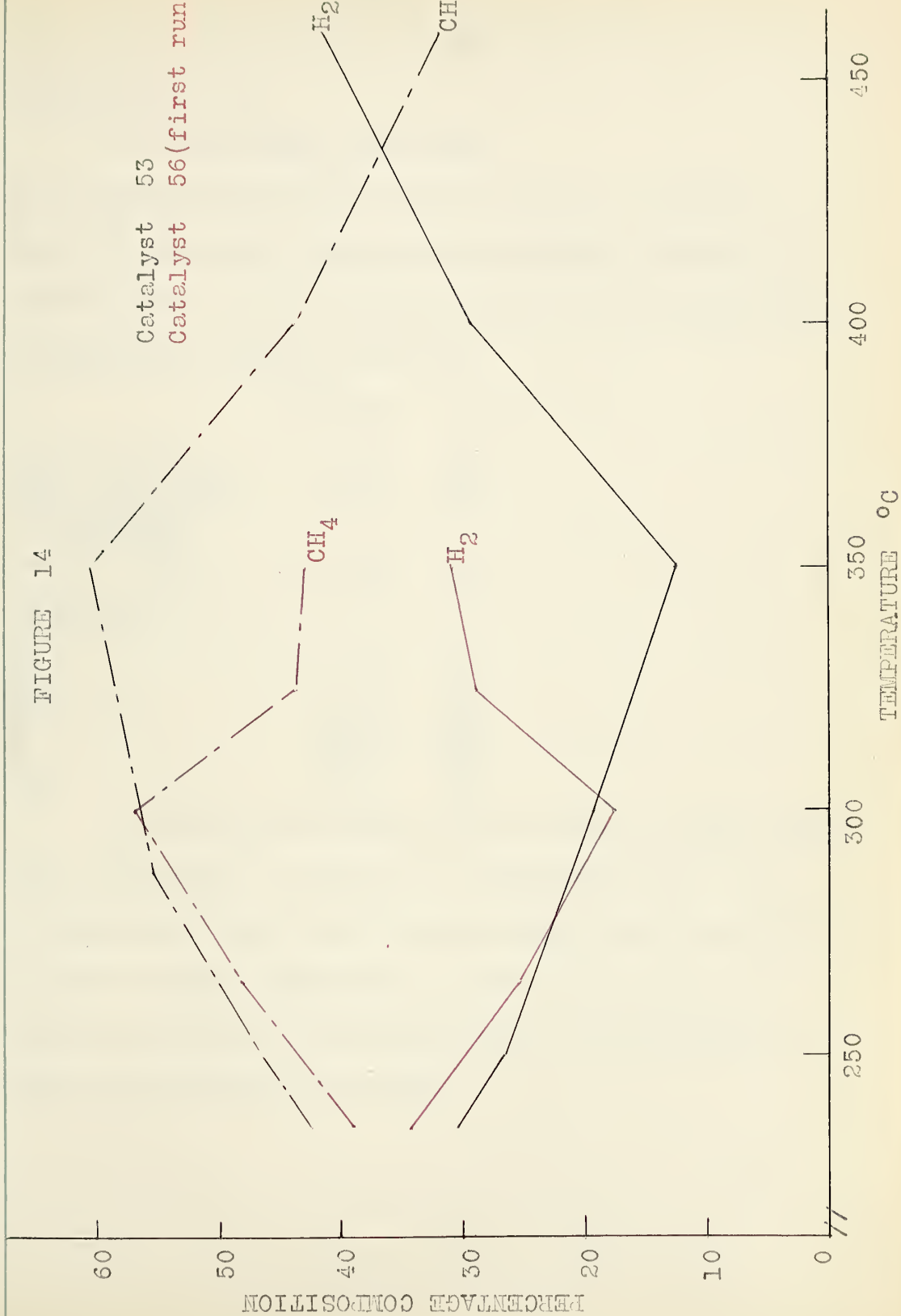


FIGURE 14

Catalyst 53
Catalyst 56 (first run)



Catalyst number 54.

contained 50% of each oxide.

This catalyst behaved quite differently than the preceding members of the series. Although the fundamental reactions were much the same, there is an apparent absence of CO decomposition as shown by the results in table 49.

T A B L E 4 9.

Temperature °C	280	385
Liquid flow cc/min.	0.75	0.75
Ratio <u>Liquid in</u> <u>Liquid out</u>	-	-
Gas flow cc/min.	150	320

Gas Analysis.

CO ₂	9.1	4.7
C ₂ H ₄	1.1	0.0
H ₂	39.4	41.3
CO	17.2	22.9
CH ₄	33.2	31.2

The gas flow was small and intermittent at lower temperatures. The action of chromium as a dehydrating agent is conspicuously small and it will be noticed again that the percentage is lower at higher temperatures. No doubt this is due to the increase in activity of the nickel without a corresponding increase in the activity of chromium.

Catalyst number 55.

contained 40% nickelic oxide.

This catalyst was relatively inactive at low temperatures. As in the last example the decomposition of acetaldehyde was not as complex as usual, nor was carbon deposited to any great extent, these points are clearly indicated in table 50. It is evident that the chromium, being present in larger quantities, serves mainly to inhibit the activity of the nickel and prevent CH_3CHO and CO decompositions as secondary reactions.

T A B L E 5 0.

Temperature °C	350	400
Liquid flow cc/min.	0.75	0.75
Gas flow cc/min.	120	320

Gas Analysis

CO_2	2.5	1.8
C_2H_4	1.1	0.0
H_2	69.5	51.7
CO	6.0	22.3
CH_4	20.8	24.1

Catalyst number 57

contained only 9% nickelic oxide.

This catalyst was much less active than any others in this series giving a gas flow of only 20 cc/min. at 325° and 40 ccm. per minute at 400°, with the following composition:

CO ₂	3.6
C ₂ H ₄	4.6
H ₂	64.7
CO	13.2
CH ₄	14.0

Practically no carbon was deposited upon the catalyst at the end of the experiment.

The dehydrating action of chromium is more evident in this case, but apparently nickel even in small amounts is much more active and has a greater influence on the decomposition approaching promoter action.

Catalyst number 58.

contained 53% nickelic oxide which had been precipitated with ammonium hydroxide.

The results with this catalyst are not tabulated since they correspond very closely to those obtained with catalyst 54 which contained 50% nickel. They illustrate, in this case, the independence of the properties of the catalyst with regard to the precipitating agent. This is not necessarily a general rule, however, and as shown in other cases, the precipitating agent may have a quite definite influence on catalytic activity.

The dehydrating action of the chromium present in the mixed catalysts having been so thoroughly suppressed, it was thought that the ultimate form of the chromic oxide might have been one of those mentioned by Sabatier as essentially dehydrogenating.

Catalyst number 59.

prepared by precipitation with KOH of chromic hydroxide from a solution of chromic nitrate. The precipitate was washed thoroughly and dried at 110°.

The results are indicated in table 51.

T A B L E 5 1.

Temperature °C	340	420
Liquid flow cc/min.	0.75	0.75
Ratio <u>Liquid in</u> <u>Liquid out</u>	-	1.1
Gas flow cc/min.	340	500

Gas Analysis.

CO ₂	5.5	8.7
C ₂ H ₄	18.0	30.4
H ₂	54.4	51.0
CO	1.4	nil
CH ₄	20.7	8.2

These results partially verified the dehydrogenating activity at 340° the catalyst was only 25% dehydrating and 60% dehydrating at 420°. It was previously noted that the yield of ethylene decreased with rising temperature in the mixed catalysts but in the above case the reverse is true. This indicates that in the mixed catalysts the activity of the nickel increases more rapidly with temperature than does the activity of the chromium. The nature of the side reactions on this catalyst are rather difficult to interpret in view of the small production of CO

and free carbon. Obviously chromium inhibits aldehyde decomposition, but it also seems to promote hydrogenation of the oxides of carbon.

Catalyst number 60.

Pure nickelic oxide prepared by precipitation of the hydroxide from a solution of nickelic nitrate. The precipitate was washed and dried at 110°. The results are shown in table 52.

T A B L E 5 2.

Temperature °C	270	285	300	350	400
Liquid flow cc/min.	0.75	0.75	0.75	0.75	0.75
Ratio Liquid in					
Liquid out	-	-	-	-	2.2
Gas flow cc/min.	180	375	425	500	500

Gas Analysis

CO ₂	14.7	21.2	20.6	21.2	20.3
C ₂ H ₄	2.1	2.0	0.8	2.6	nil
H ₂	48.9	51.8	53.4	40.8	43.8
CO	11.4	4.8	4.6	6.2	5.5
CH ₄	23.0	20.1	20.6	29.2	30.5

These results are very much as expected, showing an action of at least 97.5% dehydrogenating. The ratios of products are very similar over the temperature range and the irregularity of ethylene content suggests some outside influence on the decomposition. The formation of carbon on the catalyst was not as large as the CO₂ content of the gas would indicate, and some of the CO₂ was apparently formed by another reaction. It was noticed that the catalyst was very sensitive and lost its activity rapidly; subsequent runs to those shown in table 52 produced gas flows of the order of one-half the tabulated values, although the composition was much the same.

The differences in catalytic activity of the simple and mixed catalysts is evident from a comparison of the results presented. With the mixed catalysts there were certain ranges of temperature in which a decided change in catalytic action, and possibly catalyst surface, occurred. The quantities of carbon dioxide and methane reached maxima at this temperature on the mixed catalyst, while with the single metal catalysts they are at a minimum. The amount of hydrogen reaches a minimum on the mixed catalyst and a maximum on the simple catalysts in the same temperature range. This seems to indicate a more simple reaction on the single catalysts involving to a large extent only decomposition of acetaldehyde subsequent to dehydrogenation.

Another series of catalysts were prepared by the ignition of equimolar solutions of nickel and chromium nitrates alone and on various supports.

Catalyst number 61

prepared by soaking long fibre asbestos in the nitrate solution and igniting in a muffle furnace at 1000°.

Catalyst number 62

prepared by evaporating the equimolar solution to dryness and igniting the mass.

Catalyst number 67

Similar to 61 with the substitution of porcelain chips for the asbestos.

Catalyst number 68.

Prepared by a fresh alumina gel in a solution of the nitrates and igniting at 1000°.

Catalysts 61 and 67 were very inactive with a gas flow of only 35 ccm. per minute at 450°, and indicating very slight aldehydic decomposition. Catalyst number 62 was not quite as inactive, but it produced only 70 ccm. per minute of gas. Catalyst number 68 was entirely inactive. The results of these catalysts are summarized in table 53.

T A B L E 5 3.

Catalyst No.	61	62
Temperature	450	450
Liquid flow cc/min.	0.75	0.75
Ratio <u>Liquid in</u> <u>Liquid out</u>	1.2	1.6
Gas flow cc/min.	35	70

Gas Analysis

CO ₂	1.8	1.3
C ₂ H ₄	4.4	13.4
H ₂	87.0	66.0
CO	0.6	6.5
CH ₄	6.2	12.7

The action of chromium is much more apparent in these catalysts and indicates the greater sensitivity of nickel to

harsh treatment. This inactivity on the part of catalysts prepared by ignition was not unexpected in view of the work of Taylor and Burns reported by Bancroft (7), and Gilfillan (56); but more than this, it is seen that in these mixed catalysts the constituents are affected in a widely varying degree. Supported catalysts frequently show an increased activity, due to the exposure of more active points on a larger surface area, but in the examples investigated the reverse is more nearly true. These mixed catalysts do not behave as though each metal were exerting its influence altogether independent of the other. The catalyst surface apparently retains only a portion of the activity of the individuals and on ignition may lose all but a slight activity. On the ignited catalysts, two distinct primary reactions occur as a result of this residual activity indicating that the catalyst is now a mixture of two independently active materials. The secondary decompositions of aldehyde and CO do not occur to a very appreciable extent, possibly again indicating the inhibiting action of chromium as well as the marked decrease in the activity of nickel.

The effect of precipitating equimolar nickel and chromium hydroxides on supports was investigated with three catalysts.

Catalyst number 63

Prepared by soaking porcelain chips in an equimolar solution of nickel and chromium nitrates and subsequently boiling these chips in KOH. The solution was drained off and dried at 110° . It contained an excess of alkali.

Catalyst number 65

Prepared as with 63, but the excess KOH was removed by thorough washing, after which the catalyst was dried.

Catalyst number 69

Prepared by soaking a fresh alumina gel in an equimolar solution of nitrates and treating with hot concentrated KOH. The mass was washed thoroughly and dried at 110° .

These catalysts were slightly more active than those prepared by ignition, but they were not nearly as active as the unsupported catalysts. Catalyst number 63 produced 10, 20 and 25 cc. per minute of gas at 350° , 450° and 500° respectively, with an almost identical composition. The absence of alkali seemed to make catalyst 65 slightly more active, and an appreciable amount of ethylene was produced or survived in the absence of the alkali.

Attempts with catalyst 69 met with much more success, and it was considerably more active. The actual analytical results obtained with these three catalysts are indicated in table 54.

T A B L E 5 4.

Catalyst No.	63	65	69	69
Temperature °C	450	450	325	450
Liquid flow cc/min.	0.75	0.75	0.75	0.75
Ratio Liquid in				
Liquid out	1.2	-	-	-
Gas flow cc/min.	20	35	90	210

Gas Analysis.

CO ₂	2.2	1.0	2.3	2.8
C ₂ H ₄	5.4	10.0	5.0	7.7
H ₂	86.7	82.0	72.0	64.1
CO	1.0	1.5	13.0	10.3
CH ₄	4.7	5.5	7.7	15.0

Attempts to activate catalysts 63 and 65 by steam treatment met with no success. As with the ignited catalysts, these analyses indicate that the use of a supporting material has caused a fundamental alteration in the activity of the catalysts, with the result that the nickel and chromium are again behaving as catalytic individuals and appear to be acting quite independently of each other.

D I S C U S S I O N.

The conclusions which may be drawn from the results of this work have been evident in the presentation and only a gross summary will be made.

The change in properties of catalysts with change in reaction temperature is of common occurrence and is evident in these catalyst mixtures. There is a well defined temperature region in which a marked change in the catalytic action occurs. This may be due to changing activity of the nickel or to a new effect which can be attributed to the mixture of catalysts as a whole.

In mixed catalysts of this type it is evident that the activity and the nature of the reactions depend largely upon the method of preparation. This work indicates that the activity of the chromium is not evident compared to that of nickel, unless the catalyst has undergone severe treatment. Nickel is much more sensitive to vigorous treatment than chromium.

There are a variety of reactions possible and apparently the number and nature of the reactions that occur is a function of the history of the catalyst as well as being dependent on the temperature. In two cases the nature of the reducing agent is of importance in determining the course of secondary reactions.

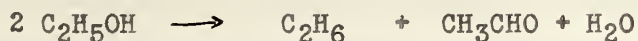
Generally the most active catalysts for the primary reaction also promote the secondary reactions, but the action of chromium in excess in these catalysts seems to be an inhibition of this tendency.

The formation of Ethane.

Previous workers have noted the presence of ethane among the products of the catalytic decomposition of ethyl alcohol, and two mechanisms have been advanced to account for its presence.

Engelder (44) has suggested that it is due to the hydrogenation of ethylene produced when using a catalyst which acts both in a dehydrating and dehydrogenating manner. Dehydration yields ethylene and water; dehydrogenation yields hydrogen and acetaldehyde and at higher temperatures the latter will undergo further decomposition to methane and carbon monoxide. The amount of water produced will indicate the extent of dehydration.

The second mechanism is due to Adkins (10) who proposes a reaction that yields ethane directly in a primary reaction as follows:



It should be possible in certain cases to determine whether the reaction which yields ethane is a primary or a secondary step.

Table 2 shows the formation of ethane over catalyst No.

16 containing Zn and Cr, and from a study of the gas analyses alone, it seems apparent that it is formed by a primary reaction. Secondary reactions are promoted by a slow space velocity, but in this case the larger quantity of ethane is formed at the higher rate of passage. The hydrogen concentration is practically identical in both cases and is actually larger when the larger quantity of ethane is indicated.

The results in table 5, on catalyst No. 22, seem to point to the source of ethane as hydrogenation of ethylene. With increased ethane production the ethylene content is reduced, and in view of the fact that all of these runs were made at the same space velocity, the hydrogenation mechanism seems most probable.

Catalyst 28 A, with the results shown in table 8, seemed to merit further study along this line, and the condensates were studied rather carefully. These results show quite clearly how the catalyst changed from a dehydrating agent at 350° to one possessing considerable dehydrogenating power at 500° C. It will be noticed that the percentage of ethane increased while that of the ethylene decreased with rising temperature. This would seem to indicate that the ethane was due to the hydrogenation of ethylene, were it not for the fact that Pease and Durgan (54) have shown that the dehydrogenation of ethane is favored with an increase of temperature.

The hydrogenation of CO and CO₂ is quite definitely favored by an increase in temperature, and this reaction is evident in the analyses. The actual analysis of the condensates obtained by fractionation gives the amount of water recovered, and this may be compared with the quantity of water that entered the reaction tube plus the water produced in the reactions. This comparison is given below in table 55.

T A B L E 5 5.

Temperature °C	350	400	450	500
Vol. of alcohol solution ccm.	36.4	29.9	8.3	29.6
Condensate, ccm.	23.5	20.0	7.0	12.0
Alcohol decomposed ccm.	12.9	9.9	1.3	17.6
Water in alcohol solution	7.3	6.0	1.7	5.9
Water from dehydration based on ethylene	3.8	2.4	0.2	3.1
Water calculated on ethane formation	0.1	0.1	0.1	0.7
Total calculated water	11.2	8.5	2.0	9.7
Water found	11.5	8.7	2.5	10.2
Positive error ccm.	0.3	0.2	0.5	0.5

The water originally present in the solution did not undergo reaction and consequently the figures in the fifth row are permissible. It was noted that all of the condensates were acidic in nature and also contained a small quantity of oil. These products will be mentioned in the discussion on the formation of carbon dioxide. The excess quantity of water noted may be at least in part due to hydrogenation of CO or CO₂.

It seems quite evident from these results that the source of ethane with this catalyst was at least in part through the reaction of Adkins. Although the water balance would be the same by either mechanism, the other factors which must be considered relegate the hydrogenation theory to a doubtful position in this series of experiments.

The results with the other silica catalysts are not in sufficient detail for the purposes of quantitative calculation, but show qualitatively a similar conclusion.

Catalyst number 33 C, with results given in table 22 is also one of the catalysts which promotes the primary reaction for the formation of ethane. The catalyst is dehydrogenating as shown by the excess of H_2 , but the extremely small amounts of ethylene would seem to indicate that this gas was not formed and hence the ethane was produced directly. The catalyst, after oxidation and reduction, promoted the hydrogenation of carbon oxides, but the small ethane content indicates that the reaction which produced it was inhibited by this treatment. Such a result might have been predicted from the original result at 500° which showed less ethane than the run at 275° . This seems to indicate that Adkins mechanism is rather sensitive to vigorous treatment of the catalyst.

The results with the three promoted chromium catalysts, table 26, are extremely interesting. In all cases the ethane is

undoubtedly the result of hydrogenation of ethylene. From the table of relative catalytic activities given in the introduction, it will be observed that both molybdenum and titanium behave as mixed catalysts, with the latter about 68% dehydrating, and the former only 23% dehydrating. The action of lead has not been investigated in this work, but Madenwald, Hencke and Brown (58) found PbO extremely efficient in the reduction of Nitrobenzene to aniline, and therefore it might be expected to behave as a hydrogenating catalyst. All of these results have been clearly verified with these catalysts and the effect of promoters is excellently illustrated. Since the hydrogenation of ethylene has been carried so far with the PbO promoted catalyst, this seems to make it exceptionally satisfactory as a hydrogenating medium.

These results show clearly that ethane may be produced during the decomposition of alcohol by either or both of two reactions. The primary formation of ethane, acetaldehyde and water occurs without doubt, and on some catalysts nearly exclusively. On occasion, the primary reaction produced ethylene, which may be hydrogenated to ethane. Both reactions may occur simultaneously on the same catalyst.

The formation of Methane.

Methane is found very frequently among the products of the catalytic decomposition of ethyl alcohol, but it has apparently not been recognized that there are several possible reactions by any of which this hydrocarbon might be readily formed.

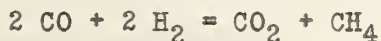
As has been previously pointed out, the dehydrogenation of alcohol to acetaldehyde may be followed by the secondary decomposition of the latter to CO and CH₄ with a great variety of catalysts (78a).

Another possible source of methane as a result of the above reactions is the well known water gas reaction

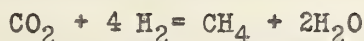


This reaction has been variously investigated. For example, Sabatier (80a) worked with nickel and found that the reaction commences at 180 - 200° and goes rapidly without complications at 230 - 250°. The catalyst being only slightly carbonized. If there is an excess of CO the reaction does not carry on to completion, some unchanged hydrogen being noted. Above 250° much of the CO is decomposed to C and CO₂ and some of this latter may itself be hydrogenated. Sabatier and Senderens (78) also investigated the action of many other catalysts and found that copper, iron and platinum were without action, while nickel, cobalt and palladium promoted the above reaction. This reaction was investigated by many other workers and Armstrong and Hilditch (59) pointed out

the fact that water gas containing hydrogen and carbon monoxide (purified from sulfur compounds, etc.) reacted over many catalysts to produce CO_2 and methane



Using CO_2 with hydrogen the reaction was the usual one, leaving unaffected any CO_2 in excess



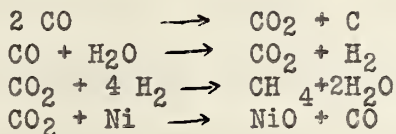
Nickel was found to be the most active catalyst, cobalt also being quite active. Silver was inert, iron nearly so, and platinum and palladium relatively inactive. Various couples were also investigated possessing varying activity, all less than pure nickel. Chakravarty and Ghosh (62) also worked with a nickel catalyst and made several interesting observations. They found over a wide range of space velocity that all of the CO was used. Their catalyst entirely suppressed the decomposition of CO yielding carbon; the CO_2 which was produced was mainly from $2\text{CO} + 2\text{H}_2 = \text{CO}_2 + \text{CH}_4$ and partly from $\text{C} + 2\text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2$. A later paper discussed a wide variety of catalysts at 300° including Ni, Mn, Zn, Pb, V, Cr, Mo and Al. Catalysts containing the last element were most promising, although carbon was invariably deposited.

Carbon dioxide is also quite readily hydrogenated over nickel to form methane:

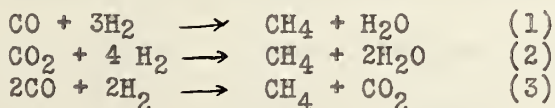


The reaction begins at a higher temperature than with CO but is fairly rapid around 300° and does not offer any complications up to 400° (78a). When hydrogen is in excess the CO₂ disappears completely. This merely confirms the results of Armstrong and Hilditch previously mentioned.

Neumann and Jacob (69) investigated the equilibrium relationships in the formation of CH₄ by the hydrogenation of CO or CO₂. The results indicated many complications at as low a temperature as 390°. Some of these reactions are as follows:

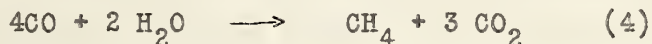


Hightower and White (64) have summarized the work done on mixtures of carbon monoxide or dioxide with hydrogen, and have investigated these reactions once again employing nickel as the catalyst at temperatures of 280 - 370°C. The results agree with previous work and also note that the secondary decomposition of CO is quite small. There are three reactions generally accepted



and these reactions depend upon several conditions. The reaction with CO₂ appears to be uncomplicated, but the reactions involving CO seem to depend quite largely upon the amount of water vapor present. Water vapor appears to have a marked repressing action

on (1), and the removal of water vapor seems to promote reaction (2). They remark on the possibility of the reaction



and conclude that it is impossible to calculate the exact path of the reaction.

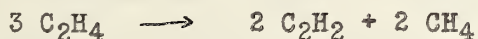
The above mentioned action between steam and CO has been investigated by Vignon (79) who, using nickel turnings as a catalyst at 400°, obtained 12.5% CH₄. Copper gave a 6.3% at 700° but nothing at 500°. Silica, alumina and magnesia behave likewise in producing CH₄ at a high temperature. These results are not in agreement with those of Pascal and Botolfsen (70), who investigated the reaction using a Ni catalyst. They found up to 275° that the yield of methane was quantitative and at 300° the reaction yielding CO₂ and H₂ was appreciable. At 750° CH₄ is entirely absent. At higher temperatures the production of CO and H₂ is favored and reaction (4) is suppressed.

A recent paper by Razuivaev (77) on the paraffinization of alcohols considers aldehyde decomposition, and the water gas reaction as the only sources of methane.

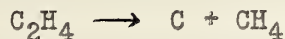
The experimental results obtained in the present work suggest that the reactions reviewed are not sufficient to account for all of the methane produced in alcohol decomposition. There

are at least two other possible sources of methane. The first of these is the pyrolytic reaction of ethylene in the presence of hydrogen. Ethylene is noted among the products of the catalytic decomposition of ethyl alcohol and frequently it is associated with methane.

The action of heat on ethylene has been investigated by Day (63) who found that it is stable at 344° but undergoes considerable decomposition at 570°. Bone and Coward (60) have given a very complete indication of the possibilities of decomposing ethylene by heat. As a result of their work they concluded that the mechanism suggested by Lewes (66) of



did not satisfy their experimental results, nor was Marchand's (67) mechanism,



supported by their experiments.

The quantities of methane produced from ethylene at 570 - 580° increased with time amounting to 15.2% in 15 minutes, 38.8% in 150 minutes. Ethane was 8.0% in 15 minutes, but only 2.9% in 150 minutes. Less than 1% of the carbon present in the original gas is thrown down as free carbon.

More recently Pease (71) has investigated the non-catalytic

polymerization of ethylene at 450 - 600°. He also notes that the quantity of methane increases with the time of heating. At the lower temperatures methane and ethane are formed in nearly equimolar quantities, but at higher temperatures the methane is in excess. Small quantities of methane were also noted in the hydrogenation experiments, although ethane was largely present.

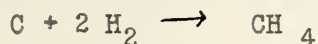
Experiments on the catalytic decomposition of ethylene carried out by Sabatier and Senderens (75 a, b) with nickel above 300° indicate that the ethylene disappears forming free carbon, hydrogen, ethane and methane. At higher temperatures the percentage of ethane decreases. Cobalt behaves much the same; iron is slow, and platinum and copper relatively unreactive. Catalytic hydrogenation also gives methane, as shown by Sabatier and Senderens (75 b) and Ipatiev and Kliukvin (65), the former using cobalt and the latter alumina in the presence of ethyl alcohol. Ethane, however, is the principal product.

Cantelo (61) also worked on the catalytic decomposition of ethylene at the surface of nickel, and his results are mainly in accord with those of the other workers. He found, however, that ethane was stable up to 350° which is in disagreement with Sabatier (75 a).

Experiments were carried out at temperatures from 150° to 350° and indicated 32.9% CH₄ and 47.0% C₂H₆ at 300°. No results

were given for experiments below that temperature. 350° indicated 40.2% CH₄ and only 36.7% C₂H₆.

Cantelo investigated the methane equilibrium

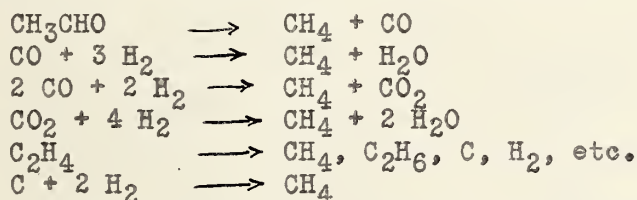


and found 50.4% CH₄ at 510° down to 20.3% at 615°. These results are roughly in agreement with Mayer and Altmayer (68) who worked with cobalt and nickel. Equilibrium conditions for this reaction as shown by Mayer and Altmayer indicate 98.8% CH₄ at 250°, 62.5% CH₄ at 500°, and 6.1% CH₄ at 750°. This equilibrium, without a catalyst, has been investigated by various workers, Bone and Coward (60), Pring and Fairlie (73), Cantelo (61), Randall and Mohammad (75) and others, at high temperatures and various pressures. The results indicate in the case of Pring and Fairlie that an initially higher yield of methane is obtained with amorphous carbon than with graphite, due to the fact that true equilibrium is reached with the latter while the carbon is slowly changed over to the graphitic form thus delaying the equilibrium.

In connection with this reaction some of the possible sources of carbon should be indicated. The decomposition of CO into carbon and CO₂ has already been indicated, as has the formation of carbon in the deposition of ethylene. Randall and Gerard (74) and Randall and Stuffer (76) have also pointed out the possibility of formation of small quantities of carbon in the reaction between carbon dioxide and hydrogen. These possibilities

are nearly always present, and hydrogen is also invariably found among the products, indicating reasonable chance for this source of methane.

There are then six possible reactions forming methane in the catalytic decomposition of ethyl alcohol



It seems probable that any or all of these reactions may occur, although it should be possible in some cases to eliminate certain reactions from the range of possibility and narrow the field to some extent.

The complexity of the reactions is evident, and consequently a complete and satisfactory explanation of the source of the methane observed among the products is very difficult to establish, but the reactions vary distinctly with the type of catalyst used and are in general accord with the results expected from other experiments.

In the following discussion only a few of the reported results have been submitted to a careful scrutiny, but these are typical examples and the results not dealt with here can be explained in a similar manner. The action of nickel has already

been discussed in detail, and the results shown in table 1 confirm this completely. Dehydrogenation followed by the secondary reactions involving aldehyde and CO decomposition produces CO_2 , CO, CH_4 and H_2 , as the products. Calculating the CO_2 produced as CO decomposed gives an analysis as shown in table 56.

<u>T A B L E</u> <u>5 6.</u>				
Temp.	CO_2	CO	Total as CO	CH_4
330	0.8	25.7	27.3	28.6
375	19.5	5.5	44.5	42.5
400	21.8	3.4	47.0	50.0
450	23.4	4.4	51.0	48.6
500	20.6	2.0	43.2	45.2

It is obvious from the balances obtained that the methane is produced directly from the decomposition of aldehyde and hydrogenation of CO or CO_2 is inappreciable.

Hydrogenation of CO_2 on a small scale is illustrated with catalyst 22, shown in table 3, in which small quantities of methane are indicated at increasing temperature. The absence of CO throughout, coupled with the fact that hydrogenation is favored with rising temperature, make this reaction quite evident. There was no evidence of carbonization on the catalyst and the excess of water decreases the tendency to hydrogenate CO (64) and it seems improbable therefore that there was any aldehydic decomposition. As has been previously mentioned, ethylene produces

carbon and ethane, as well as methane and hydrogen, and the absence of these former products makes this source of methane impossible.

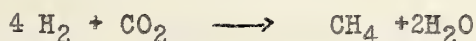
Another set of interesting results were those obtained with catalyst number 28A given in table 8. These have already been discussed in the production of ethane. Undoubtedly some acetaldehyde has been decomposed, but polymerization or decomposition of ethylene is improbable as has been shown in the previous discussion. The large excess of CO_2 over CH_4 necessitates some other source of CO_2 than CO produced from acetaldehyde. The formation of CH_4 in this experiment can only be due to hydrogenation of CO_2 . From table 55 the water balance obtained indicates an excess in every case, and this increases with rising temperature or with the methane content, and consequently the formation of water and CH_4 by hydrogenation of CO_2 seems a quite probable reaction.

It is realized that if any ethylene was decomposed this would also introduce a positive error in the water balance, but the ratios of methane to ethane in each case preclude this reaction taking place in the light of the work of the investigators previously mentioned.

Table 10, which indicates results obtained with catalyst 28C offers interesting possibilities. Two sources of the methane

obtained at 400° and 450° are offered; hydrogenation of CO₂ and decomposition of ethylene. The action of the nickel in this catalyst is quite evident, but it was expected that the hydrogen content of gases would increase with temperature as in table 8. The results with the nickel-chromium series show nickel to be more active than chromium, and in the copper chromium catalyst, No. 28A, chromium was more active than copper.

The explanation of the anomaly may be found in the hydrogenation of CO₂ which requires 4 volumes of Hydrogen for each volume of methane produced.



With a temperature increase from 350° - 400° the ethylene content also increases, but at 450° there is a surprising decrease and at the same time the CO₂ and CH₄ percentages increase. This seems to suggest that some of the ethylene formed is decomposed and includes methane as one of its products with no ethane. The decomposition of aldehyde is evidently not of appreciable magnitude.

One of the experiments conducted with CO₂ and alcohol on catalyst number 33 A, table 19, indicated the formation of CH₄ both in aldehyde decomposition and by hydrogenation of CO and CO₂. In this case the excess of CO₂ in the gases seemed to accelerate the formation of CH₄. The decrease in the percentage of methane with an increase in temperature may be due to a decrease in activity

of the catalyst for the hydrogenation reaction, or to the fact that more of the aldehyde undergoes a decomposition involving the formation of CO_2 . This latter suggestion is in accord with the increased CO_2 production at 450° , and the decomposition of acet-aldehyde in this manner will be discussed later.

A similar conclusion to that drawn above, holds with the nickel chromate catalyst No. 38, table 28, using CO_2 and alcohol. This is particularly evident when the runs at 350° and differing space velocities are compared. In the case of the lower rate the methane content is considerably higher, while the hydrogen and carbon dioxide productions are lower.

With the nickel chromium series, the graphs bring out quite clearly the relationship between hydrogen and methane. The CO_2 curve is roughly similar to the methane line and indicates that an increasing percentage of CO_2 accelerates the hydrogenation reaction involving a hydrogen decrease and a methane increase.

The above results have been selected as showing that methane may be formed during the decomposition of ethyl alcohol by two other reactions in addition to those commonly accepted. Quantitative determination of the extent of each reaction is impossible because of the number of concurrent reactions. In those experiments where there is little doubt that ethylene may be a source of methane, and in the experiments in which CO is produced and decomposed to C and

CO₂, methane may be synthesized from its elements.

THE FORMATION OF CARBON DIOXIDE.

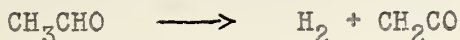
Several mechanisms have been offered to account for the appearance of carbon dioxide among the gaseous products of the catalytic decomposition of ethyl alcohol and mixtures of alcohol and water.

The oxidation of CO by steam (79) and the decomposition of CO to C and CO₂ (86) have already been discussed. Sabatier and Mailhe (26a) have shown that oxide catalysts may be reduced by ethyl alcohol vapour and CO₂ and acetic acid produced. Obviously this reaction ceases when the oxide has been completely reduced. Moreover the hydrogenation of CO as previously discussed (64) may yield CO₂.

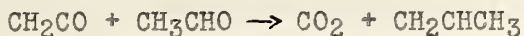
Brown and Reid (41) have suggested that CO₂ is due to the condensation of acetaldehyde producing an ester, which on decarboxylation yields CO₂ and an hydrocarbon. The decarboxylation of ethyl acetate has been reviewed by Sabatier (87) and further investigated by Adkins (34) and found to proceed readily over certain catalysts. Armstrong and Hilditch (47) have reported the presence of ethyl acetate among the liquid products of the reaction of ethyl alcohol over nickel at temperatures above 350°C. In view of the fact that acetic acid has been reported so frequently as a product it seems quite possible that the ester

would be formed directly in many cases. If this is so, the decarboxylation as mentioned above, would form another possible source of CO_2 .

Lazier and Adkins (37a) believe, however, that none of the above mechanisms are satisfactory. Several factors must be taken into consideration. These include the presence of carbon dioxide, the acidic nature of all condensates and the frequent observance of a brown, water-insoluble resin. These workers proceed to develop a mechanism which will account for all of these facts. Lazier and Adkins suggest that the catalyst employed is dehydrogenating and the aldehyde produced by this reaction is still further dehydrogenated to yield a ketene.



The reaction between this ketene and more of the aldehyde would produce CO_2 and an unsaturated hydrocarbon.



which would probably polymerize to produce the resin so frequently noted. The reaction between the ketene and water would produce the acetic acid frequently noted among the products of the decomposition of ethyl alcohol; while the reaction between this ketene and alcohol itself produces ethyl acetate. Incidentally, this paper also notes, without comment, that the presence of water increases the percentage of CO_2 and H_2 .

There are objections to the proposed reactions that are at present unanswered. Several experiments showed the production of large amounts of CO_2 under conditions which preclude its formation by decomposition of CO or the oxidation of CO by water. These experiments are of two classes, tables 3, 4, 7 and 26, for example, showing a gas largely CO_2 and H_2 , and at the same time relatively large amounts of oil of two distinct types. Tables 27, 34, 35 and 36, on the other hand, indicate CO_2 and H_2 and no oil.

The mechanism due to Lazier and Adkins might suffice for some of the former class of results, but the small quantity of higher hydrocarbons found are insufficient compared to the amount of CO_2 produced. The simplest hydrocarbon produced by Brown and Reid's mechanism, propane, was not found in any experiment. As a result two new mechanisms are proposed, and it is believed that they account for the excess CO_2 found as compared to the work reviewed above. They are not necessarily exclusive, but supplement the mechanism of Lazier and Adkins.

The reasons for such conclusions will be briefly stated before the discussion is presented. Confirmation of the possibility of the ketene reaction taking place, has been obtained, and in certain cases an hydrocarbon has been isolated with an empirical formula in the ratio C_3H_6 , possessing a high boiling point

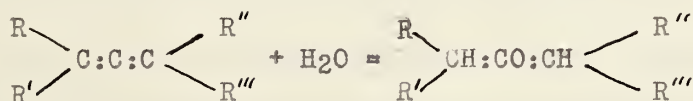
and a high molecular weight, indicating polymerization. However, in some of the experiments cited in which large quantities of CO_2 were evolved, oils were obtained which were not hydrocarbons but rather products with an empirical formula in the region $\text{C}_5\text{H}_7\text{O} - \text{C}_6\text{H}_8\text{O}$ also having high boiling points and high molecular weights, again in all probability indicating polymerization.

A new mechanism is herewith offered to account for these latter oils. This involves preliminary decomposition of the ketene forming allene hydrocarbon and evolving CO_2



Allene readily undergoes various reactions owing to its chemical nature. Lebedev (83) has reported the ease with which it is polymerized, forming compounds from the dimer to the hexamer.

He also noted that the trimer was very readily oxidized. Meinert and Hurd (85) also found polymerization of allene at $400-600^\circ$ relatively simple, obtaining 90% conversion to the liquid dimer and trimer at 500° . Allene hydrocarbons readily add on water in the presence of catalysts (81) to form ketones



in this case acetone would be formed, and Adkins (34) states that in the presence of certain catalysts acetone will condense. It is not improbable that crotonization with the formation of mesityl

oxide could occur under the experimental conditions (1). However, an additional reaction between allene and acetaldehyde would yield directly a compound with the composition C_5H_8O . This compound, which would in all probability possess the properties of an aldehyde, would accordingly be likely to condense into a polymeric form.

Such a polymer would seem to possess the properties shown by the substance formed in the reported reactions, and apparently the experimental conditions favor its formation. The slight variations in the molecular percentages shown on combustion analyses may be explained by the presence of small amounts of other substances which are possible products of the reaction. Owing to the relatively small quantities of such material obtainable in any of the experiments, a complete separation and identification is very difficult. The reactions previously outlined for the original ketene decomposition, involving acid formation, will of course still be possible.

As an interesting note, in view of the fact that certain mixed dehydrogenating and dehydrating catalysts also produce an appreciable quantity of CO, following aldehyde decomposition, in addition to ethylene, Losanitch (84) found that when a mixture of ethylene and CO was exposed to the action of the silent electric discharge, a dark brown liquid was produced which possessed a burnt odor, and on analysis indicated a composition of C_5H_8O

and seemed to be a dimer of that formula.

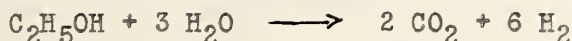
As previously mentioned, two types of oils were obtained, one with the experiments using CO_2 and alcohol as found in the experiment in table 15, on combustion analysis showed 13% hydrogen and 85.9% carbon. The relatively small quantities of ethylene present in the gas indicate that polymerization was probably the source of this product rather than a ketene reaction, since the excess CO_2 at 450° is relatively small.

When alcohol alone was used with this catalyst the oil produced was not of the above nature, but proved to be of the composition of approximately $\text{C}_5\text{H}_8\text{O}$. The boiling point of the oil was high and could not be definitely determined, but a molecular weight determination by the cryoscopic method, using benzene as the solvent, indicated a value of 230. The gas analysis indicated in table 16 indicate small CO and CH_4 content, which, in turn, shows but a slight secondary decomposition of the aldehyde. The large hydrogen content of the gas, on the other hand, indicates considerable dehydrogenation, and this seems to conform with the possibilities suggested in the above postulated mechanism, in which much of the aldehyde undergoes further reaction. The water formed by the dehydration of the alcohol might also have reacted with more alcohol to produce CO_2 and hydrogen, but this quantity would not be very considerable when compared with the other sources of gases. Analyses of the oils from the other experiments shown

in tables 3, 4, 7 and 26, gave results such as C_5H_8O , C_6H_8O , and C_6H_9O , confirming the mechanism postulated and showing it to be of frequent occurrence.

In the other new class of results, notably catalyst 37 table 27, and catalysts 44 and 45, tables 35 and 36, there was no evidence of oil formation, and yet the gas produced was essentially CO_2 and H_2 in the ratio of 1 to 4 or 5, with some ethylene. No mechanism is evident by way of acetaldehyde and ketene, unless acetone is one of the products, which was not the case.

The direct combination as follows



would produce a gas containing CO_2 and H_2 in the ratio 1 to 3. The equation as written is improbable as a mechanism, and it is necessary to divide it into steps. A primary reaction between alcohol and water yielding methanol is not beyond possibility. The reverse reaction, dehydration of methanol to form C_2H_5OH and $(CH_3)_2O$ is well known. Methanol in the presence of water at atmospheric pressure and the temperature of experiment, yields CO_2 and H_2 readily. The objection to this mechanism lies in the fact that methanol will produce CO and H_2 just as readily and no evidence of this reaction is apparent. Moreover, analyses of the distillates show methanol in very small traces, if at all, and if methanol were intermediate, it would be expected to survive in

some quantity. The condensates contained large amounts of acetaldehyde, and the excess H_2 found in the gas can readily be accounted for on the basis that only part of the alcohol was decomposed by the suggested route. In the absence of methane, CO and oils, it is evident that the decomposition of acetaldehyde was very slight.

The simple decomposition of CO to C and CO_2 is illustrated by catalyst 12, table 1, in which nickel markedly promotes this reaction and is quite obviously the source of this gas in this experiment. The possibility of any other reaction occurring in this case is extremely remote. The same reaction is also illustrated by catalyst 33 B, table 20.

It is well known that many catalytic reactions are extremely complex and from some of the results presented in this discussion the formation of CO_2 is in this class. It seems reasonable that the above mechanisms are those most likely to account for the presence of carbon dioxide, and the new mechanisms postulated fit certain of the experimental results obtained in this work.

C O N C L U S I O N S.

A detailed study of the decomposition of ethyl alcohol with water or with carbon dioxide at the surface of binary catalysts has been reported with a view to applying the results of this study in the subsequent synthesis of alcohol under high pressure.

It is evident from these results, and their subsequent discussion, that these reactions are extremely complex and secondary reactions are responsible for many of the products obtained. The analyses of the results of this research has indicated the sources of methane and ethane, and advanced a new source of carbon dioxide, in addition to presenting definite results with a large and representative selection of mixed catalysts hitherto uninvestigated.

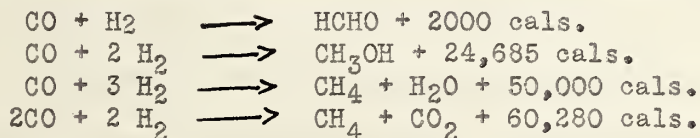
X The current theories of high pressure syntheses involve the assumption of many intermediate steps. It appears to be a reasonable conclusion that this work has further justified such a theory in view of the difficulties encountered in an effort to decompose alcohol to carbon monoxide and hydrogen. The reverse reaction, synthesis of ethyl alcohol from water gas or carbon dioxide and hydrogen would appear to be possible only through one or more intermediate steps. The occurrence of a process of this nature on one catalyst is of a smaller order of probability than the comparatively simple reactions which lead to methanol.

P A R T I I I.

Introduction.

The study of the reactions of carbon monoxide, carbon dioxide and hydrogen mixtures over catalysts at high pressure and elevated temperatures required an extensive review of previous research on this subject, and the general results of this work will be presented as an indication of the trend of these high pressure reactions.

As pointed out by Lewis and Frolich (95) the simplest reactions involving carbon monoxide and hydrogen may be written



It will be observed that the formation of methanol goes with the largest volume decrease and selective catalysts and high pressures are used concurrently, not only to shift the methanol equilibrium to the alcohol side, but also to suppress the methane reactions.

Due to its commercial importance, the synthesis of methanol has been studied very extensively (Part IV, F). The early researches involved the use of a zinc oxide catalyst which promoted the reaction, but was not very effective. The yields were improved greatly by the addition of copper.

Zinc has been shown to be a necessary constituent in a methanol catalyst and the majority of experimenters have included it in their catalysts, together with copper and chromium and specifically excluding iron, cobalt and nickel, which have been stated as favoring methane formation. Morgan, Taylor and Hedley (93), Brown and Galloway (99), Cryder and Frolich (103) have all agreed with Patart on the relative inefficiency of zinc oxide alone. The admixture of CuO and ZnO was studied by Morgan et al and found satisfactory; while Frolich, Fenske, Taylor and Southwick (98), applying some decomposition results obtained by Frolich, Fenske and Quiggle (97), found that a mixture of the oxides prepared by the co-precipitation of the hydroxides was also successful, obtaining maximum results with a catalyst containing 77% Zn. Lewis and Frolich (95) found that the addition of alumina to a zinc-copper catalyst gave excellent results, and recommended that the catalyst be supported on a good heat conductor to prevent local overheating due to the exothermal nature of the reaction.

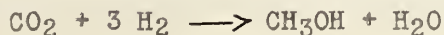
Fenske and Frolich (104) obtained high conversion with a catalyst containing zinc, copper and chromium. Morgan, Taylor and Hedley studied the activity of both normal and basic zinc chromates and mixtures of zinc and copper chromates, while Brown and Galloway (99) also investigated both types of zinc chromates, and in all of these cases the catalysts were found to promote a

satisfactory conversion of CO to CH_3OH . Plotnikov and Ivanov (106) found that the addition of Na_2CO_3 to a zinc-chromium catalyst gave better results than a catalyst prepared without the use of alkali. An explanation of the fact that a mixture of zinc and chromium oxides is more efficient than zinc oxide alone may be found in the work of Taylor and Kistiakowsky (53). The adsorption of hydrogen, CO and CO_2 on each catalyst was measured and the mixed oxide catalyst indicated greater adsorptive capacity.

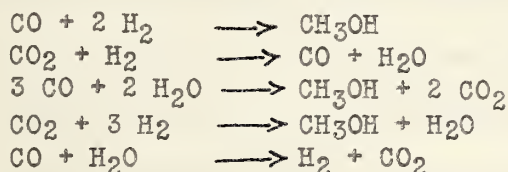
Mixtures of zinc and many other metals, including Ag, U, Cd, Mn, Mo, W, V, were tested by Morgan and co-workers with varying results. Audibert and Raineau (91) worked with a number of catalysts and found Zn and Cu the most active, with Cr and Mn also favorable with a lower efficiency, while Ni promoted side reactions.

In practically all published results, iron, cobalt and nickel are stated to be detrimental to the synthesis of methanol, but among the innumerable patents, a large number claim the successful use of these metals, usually adding a promoter to prevent carbon formation.

The above mentioned catalysts refer to the synthesis of methanol from CO and hydrogen, but mixtures of CO_2 and hydrogen also yield methanol at the surface of some catalysts (90). The reaction is evidently



since water is usually found to be about 50% of the liquid obtained. Although this reaction is used commercially, and many patents have been issued, there has been only one paper published on experimental results. Smith and Hirst (110a) with a zinc-chromium catalyst at 304°C obtained indications of five reactions



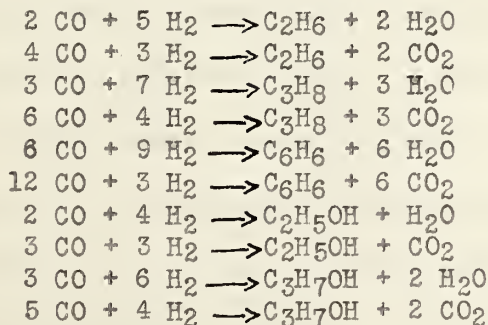
It was not found possible to determine which reaction comes nearest to equilibrium under the experimental conditions. However, as most methanol catalysts produce CO₂ or water, or both, along with methanol, it is possible that the mechanism of formation of methanol from CO and hydrogen may not be as simple as that indicated by the first equation, especially as a steady state is approached.

Adkins and Perkins (107) found distinct indications of dimethyl ether when decomposing CH₃OH over ZnO, while in the synthesis reaction with a copper chromium catalyst, Brown and Galloway (108) found considerable quantities of ether among their products. The interest here is obvious in that dimethyl ether is isomeric with ethyl alcohol. Frolich, Fenske, Perry and Hurd (102) found that the presence of excess alkali reduced the activity of a catalyst, above the melting point of the occluded salts, and

also noted that the precipitating agent used in catalyst preparation had an appreciable influence on the activity of the catalyst.

There has been a tremendous amount of work performed in a study of the methanol equilibrium, as indicated in the bibliography, and this will not be detailed here. The latest work, that of Wettberg and Dodge (118) reviews all the previous work on the three methods of evaluating the equilibrium constant and finds a serious lack of agreement in all the results. They examine the equilibrium again and set up a new equation which is compared with the previous postulations.

There are many other combinations of CO and hydrogen theoretically possible, and before discussing the experimental efforts to obtain these products, the thermodynamic possibilities as presented by Smith (112) and Francis (113) will be considered. As additions to the four reactions mentioned by Lewis and Frolich (95), Smith adds the following:

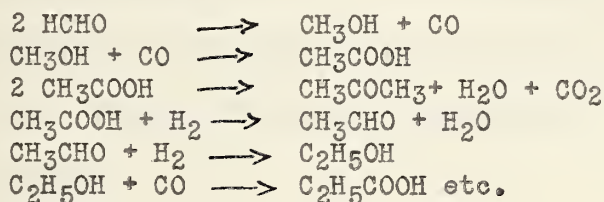


By a consideration of the free energy equations of these

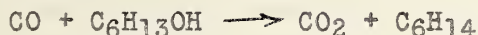
reactions the conclusions are reached that it is easier to form higher hydrocarbons than lower ones, and oxygen appears as CO_2 instead of H_2O . He cites Fischer (142) to show that once the reactions have started the tendency is to produce higher hydrocarbons, and it is difficult to produce gasoline fractions. Lower alcohols cannot be formed at atmospheric pressure and a temperature of 300° , but the higher alcohols may be produced under these conditions: while the tendency for formation of all these compounds decreased with temperature increase. Francis also concludes from similar calculations that the synthesis of gasoline from water gas can take place only below 450° .

In 1923, Fischer and Tropsch (119) announced the formation of synthetic oil mixtures, to which they applied the name "Synthol", by reducing CO with hydrogen at $400\text{--}450^\circ$ and a pressure 150 atmospheres in the presence of an iron catalyst containing K_2CO_3 . The products formed in two layers, oil and water, which on identification showed 10% as acids up to C_8 , 40% water soluble and partially soluble alcohols, aldehydes and ketones, 48% oil, volatile with steam, containing higher aldehydes, alcohols and ketones to C_9 , and the 2% residue, an oil which was non-volatile with steam. Later papers (119a) gave the most satisfactory conditions for synthol formation. The mechanisms advanced by Fischer and Tropsch (119, 120) have been critically reviewed by Jones (121)

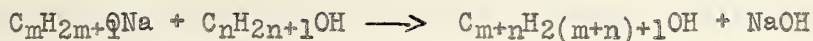
In contact with a hydrogen-carrying metal CO and hydrogen add to form formaldehyde, which may react in several ways, yielding methanol and higher alcohols. Some other possible reactions he pictures as including:



With an excess of CO in the gas mixture, a reaction such as the following is possible:



The presence of the alkali might also favor the condensation of alcoholates with alcohols.



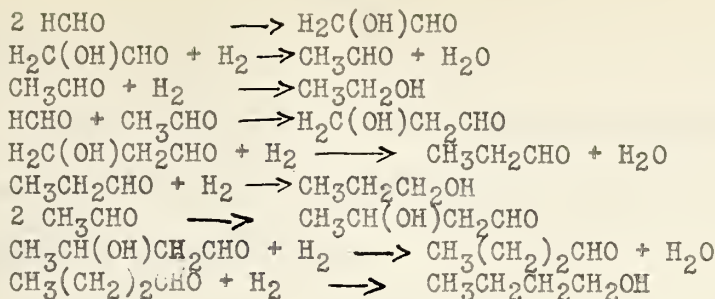
The dehydration of methanol yielding CH_2 groups which, on polymerization would add on water to form a higher alcohol should also be considered. The experimental results of Fischer's work are reviewed in great detail in "The Conversion of Coal into Oils" and will not be discussed here.

Another series of papers on the synthesis of organic compounds has originated in the Massachusetts Institute of Technology under the direction of Frolich. In 1928 Frolich (123) stated that the Synthol process, as such, was useless, due to the fact that it gave only 16.8% useful products from CO and 56.7%

was wasted. The useful products were formed in too great variety for industrial preparation. It was found (124) that an alkaline catalyst containing zinc and chromium at 460 - 490° under 240 atmospheres pressure produced a liquid containing 17.8% MeOH, 2.3% EtOH, 33.4% PrOH, 2.5% BuOH, 9% amyl alcohols and 35.6% water, while side reactions giving CO₂, CH₄ and free carbon were very hard to suppress.

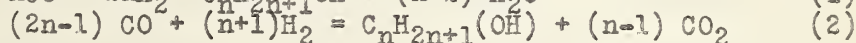
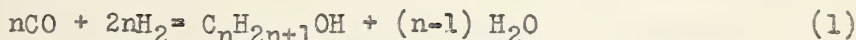
The results from the English laboratory at Teddington, as presented by Morgan and co-workers (93, 109, 128), have indicated the most positive results in the attempted synthesis of ethyl alcohol. By the addition of alkalis and cobalt to zinc chromate, they were able to produce up to 25% of higher alcohols. A catalyst containing Zn, Mn, Co and Cu, produced 79.7% MeOH, 11.6% EtOH and 7.3% higher alcohols, but the liquid contained 40% water. Zn, Cr, Co and Cu in a catalyst yielded 20.3% EtOH with water 45% of the total yield. These workers noted that Co increased other alcohols in preference to methanol, but an increase of temperature favored the latter. The results indicated that the primary product was formaldehyde, which was hydrogenated or condensed. Their experiments were conducted at a space velocity of about 30,000 and a pressure of 200 atmospheres at 380°.

The mechanisms as advanced by Morgan (109) include some of the following:



Such complex possibilities as these serve as an indication of the sources of the products and emphasize the multiplicity of reactions between CO and H₂.

Frolich (124) considers the free energy changes in two reactions:



The free energy change per carbon atom for three alcohols at 25° is given by the following:

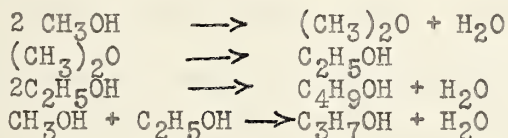
<u>Alcohol</u>	<u>Reaction (1)</u>	<u>Reaction (2)</u>
methyl	- 10920	- 10920
ethyl	- 16744	- 13577
propyl	- 18495	- 17994

From which he concludes that the character of the catalyst is the all-important factor in these synthetic reactions.

The possibility of synthesis of a wide range of aliphatic compounds exists, but the reactions must be controlled to obtain either one compound, or a limited number of single compounds, or a mixture of related compounds. Frolich concludes that studies of this type are best followed by first investigating decomposition

reactions.

Frolich and Cryder (125) advance more mechanisms for the formation of higher alcohols, involving again formaldehyde to methanol as the first steps.



The fact that ethyl alcohol is present in such small quantities suggests such step wise reductions as the above which would form higher alcohols at the expense of ethanol. These possibilities were verified by passing liquid reactants over catalysts and studying the products; methanol and hydrogen gave higher alcohols but to a lesser extent than methanol and CO. Hydrogen apparently promoted the formation of water. Methanol alone gave similar products to those obtained with CO and H₂, while ethyl alcohol had a marked tendency to form higher alcohols as suggested above. Results obtained also served as indications of the fact that esters were produced by condensation of aldehydes rather than reactions of CO with alcohols.

Water tends to reduce the yields of higher alcohols, due either to inactivation of the catalyst or equilibrium effects; while high CO concentration promotes higher alcohols, but the corresponding low hydrogen content induces dehydrogenation, and the resultant aldehydes readily condense to esters. Recently

Frolich (126) has emphasized the impossibility of any such reactions as given by Smith involving collisions of large numbers of molecules. The step-wise reactions of Fischer and Morgan are most probable.

Audibert and Raineau (122) studied the action of ferric oxide catalysts and produced hydrocarbons and alcohols. Metallic iron gave only CH_4 , CO_2 , water and small amounts of organic acids chiefly formic. Very complex catalysts containing Fe, Cu, Mn, K and P or B, also produced alcohols and hydrocarbons, of which two-thirds of the latter distilled below 180°C . With these catalysts, however, the yields were only 17%, which was not satisfactory. They conclude that the best method of studying these reactions is simply by trial due to the present empirical nature of catalytic investigations.

This review presents the most outstanding results which have been presented and indicates very thoroughly the extraordinarily complex nature of these reactions. Apparently the methods of study vary with investigators, but in both cases results are decidedly unpredictable.

In addition to the work at high pressures, a large body of literature exists on the reactions of water gas at atmospheric pressure. Following their work on Synthol, Fischer and Tropsch (119c) announced in 1926 that the higher homologs of CH_4 were

formed on passing H_2 and CO mixtures over catalysts containing iron and cobalt with various supporting materials, at temperatures of 250 - 300°. This mixture of products they called "Gasol". They believed that the catalytic processes involved the formation of a carbon-rich metallic carbide as the first stage which was reduced to methylene groups; these latter polymerized and formed saturated hydrocarbons. They also believed that this mechanism was confirmed by the fact that no oxygenated compounds were formed, all of the oxygen appearing as CO_2 or H_2O , and this fact precluded any intermediate $HCHO$ or CH_3OH formation. The products ranged from the lower saturated hydrocarbons to solid paraffins.

Elvins and Nash (141a) reported the formation of an oily product from water gas at atmospheric pressure, using a $Co-MnO_2-Cu$ catalyst, with small yields. The product included oxygen containing compounds in addition to hydrocarbons (141). Elvins (131) reported similar results and then Fischer and Tropsch (142) declared that their product also contained oxygenated compounds but in relatively small quantities. Erdeley and Nash (138) gave the results with catalysts containing mixtures of Co, Cu, Al, Mn, Zn, and Ce. The optimum oil yield was found at 280 - 290° with CO_2 and CH_4 formed above that temperature and no reaction below 230°. Co-Cu-Al was found to be the best catalyst and equal parts of CO

and H_2 the most satisfactory gas mixture. Excess hydrogen promoted water formation and excess CO reduced the activity of the catalyst. A rather indefinite paper by Hoover, Dorcas, Langley and Michelson (130) reported the formation of ethylene at 100 - 250° with 62 different catalysts. No mention was made of any liquid products being formed.

Papers by Smith, Davis and Reynolds (134), and Smith, Hawk and Reynolds (135) gave the results of a thorough study of the synthesis of higher hydrocarbons from water gas. Employing a Co-Cu-MnO₂ catalyst, saturated and unsaturated hydrocarbons from CH₄ to solids were obtained with optimum conditions yielding one gallon of fuel per 1400 cu.ft. of gas. Conversion was 18% by a single passage at 203° and increased with a higher temperature. The unsaturated compounds were increased by a higher space velocity and a higher temperature.

They make the statement (136) that the mechanisms on different catalysts are very different, even under the same experimental conditions, and one mechanism will not explain the products obtained.

This review of the three different types of reaction is not complete, but presents the current developments in these fields of research, and indicate in a general way the results to be expected in work of this nature. It is evident that ethyl

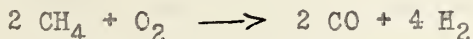
alcohol is not to be expected as a primary product, and its production in appreciable amounts has not yet been achieved.

Experimental Technique.

The gas mixtures used in this work were of two kinds, one a mixture of CO and H₂ in the ratio 1:2 approximately, and the other a mixture of CO₂ and H₂ in the ratios 1:2 to 1:2.5.

The common laboratory method of preparing carbon monoxide and hydrogen, usually termed water gas, involves the decomposition of formic acid and requires considerable equipment and attention in addition to being rather costly. In the present work, water gas was prepared directly by the partial oxidation of Viking natural gas by oxygen at 1000°C, taking advantage of methods developed in connection with other work.

Viking natural gas, with the approximate composition 94% CH₄, 3% C₂H₆ and 3% N₂, was mixed with sufficient oxygen to allow the reaction



That is, one atom of oxygen is required for each atom of carbon in the gas mixture. The proportions were very closely 2 gas to 1 oxygen by volume. The resulting water gas had the composition 65.7% H₂, 32.8% CO and 1.5% N₂ with practically no variation. The oxygen-gas mixture, stored in a 10 cu.ft. gas holder, was led over a catalyst of reduced nickel on asbestos fibre contained in

a refractory tube maintained at 1000°C or higher. Reaction was complete at this temperature with high space velocities and no CO₂ was present in the exit gas. The water gas was stored in a 20 cu.ft. gas holder pending compression.

This method was rapid and simple and required very little attention other than the preliminary mixing of the natural gas and oxygen. The flow of gas was controlled by the weights on the two gas holders and stopped automatically when the smaller gas holder was empty. The whole system was under a slight water pressure and leaks of air into the mixtures avoided. The catalyst maintained its activity over a 12 month period and was not altered in appearance. The cost of the water gas prepared in this manner is negligible and the method can be recommended where natural gas free from sulfur is available.

The mixtures of CO₂ and H₂ were prepared from commercial products. Carbon dioxide, 99% pure, was taken from a cylinder of the liquified gas. Compressed electrolytic hydrogen was obtained in the customary steel cylinders and the gas was more than 99% pure hydrogen. The gases were mixed in the required proportions and allowed to diffuse for at least eight hours before compressing.

Catalysts were reduced with either hydrogen or water gas under pressure and compressed natural gas was also available for testing or flushing the apparatus before commencing an experiment.

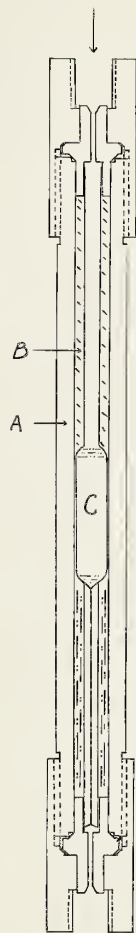
The high pressure equipment used in these experiments

requires a detailed description. A Rix, three-stage compressor adjusted to deliver gases at 4000 lbs. per square inch was used throughout the work. Before compression the gases passed over CaCl_2 in a specially built steel drying tower, and after compression they passed through an after cooler, a high pressure relief valve (155) set at 4000 lbs. to a main distributing valve. From this valve the gases could be sent through a high pressure purifying system to a secondary 4-way distributing valve. The purifiers comprised an oil trap, a CaCl_2 chamber and a soda lime chamber, which efficiently removed all impurities. The soda lime chamber was fitted with two way valves so that it could be by-passed if necessary. Alternately, the gases could be sent directly to the secondary 4-way distributing valve. This latter valve allowed the gases to be directed to a transfer line or to a 4-way valve leading to each of the four storage systems.

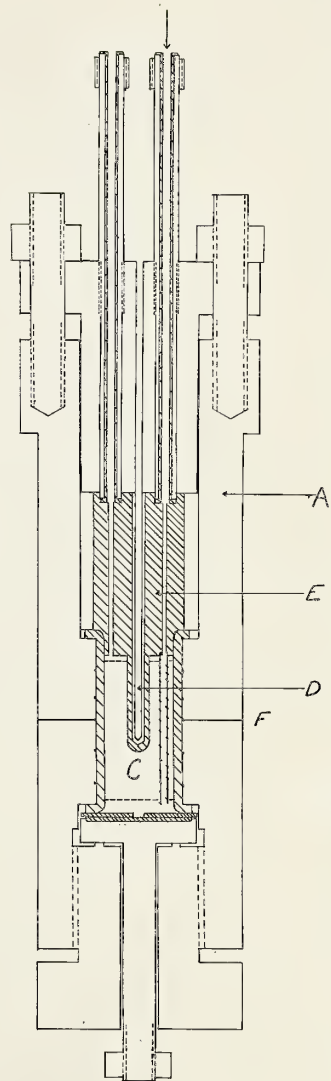
The whole storage system comprised 8 cylinders, 4 with a capacity of 5 litres and 4 with a capacity of 15 litres, and these were arranged in 4 systems each, involving a total capacity of 20 litres. Permanent storage was provided for natural gas, hydrogen and water gas, with the fourth reserved as a spare and used for hydrogen and carbon dioxide mixtures when necessary. The use of special 4-way valves made each system available to the catalyst chamber at any moment. The high pressure tubing, fittings, two-way valves, cylinder closures, etc. were of the type developed

by Ernst and co-workers (154). The four-way valves were made by combining in one body, four individual valves with a common feed. All joints were metal to metal, steel in those of small diameter and copper or aluminium in those of large diameter, to ensure the absence of leaks. Chrome-molybdenum steel tubing $\frac{1}{4}$ " by $1/16$ " was used throughout. The purifiers were fabricated from KA 2 nickel-chromium steel and the small storage cylinders of chrome vanadium steel. All fittings and the large cylinders were of carbon steel, while valve stems were made from hardened tool steel.

Two reactors shown in figure 15, approximately one-third actual size, were used in this research. The small autoclave, I A was constructed from KA 2 nickel-chromium steel. The catalyst was held in a pyrex glass tube, C. The inlet end was packed with copper turnings, B, to ensure efficient heat transfer to the gas while the outlet capillary was wrapped in asbestos paper. The reactor was heated by a split, multiple unit electric furnace. Uniform temperature distribution was maintained by a split brass sleeve fitting snugly between the furnace elements and the reactor, while the thermocouple was placed between the brass sleeve and the reactor in a groove cut on the inside of the sleeve. The difference between the thermocouple readings and the temperature within the reactor was determined and plotted; the correction to be applied varied from 8° at 250°C to 12° at 450°C . No account



I



II

FIGURE 15

was taken of any effect due to the passage of gas in view of the excellent heat transmission through metals and the good conductivity of the compressed gases.

Only a few runs were made in this autoclave, due to leakage of the gas around the glass-metal joint and the formation of considerable quantities of iron carbonyl in consequence.

The autoclave illustrated in figure 15-II is of larger size and was more satisfactory and efficient. The body was again made of KA 2 steel with the closures of chrome-vanadium steel; the inlet and outlet tubes were fabricated from tool steel and case hardened. To prevent the reacting gases from coming in contact with iron the reactor was lined with copper, illustrated by cross hatching. The well known inertness of Cu on water gas mixtures is used to advantage in this construction. Similarly the inlet and outlet tubes were lined with copper tubing. The copper block, E, was fitted with an Enduro collar to prevent jamming and the thermocouple well, D, through the copper, was lined with an Enduro tube to prevent the collapse of the well under heat and pressure. Spaced around the body of the reactor were 4 - 1/32" holes, drilled to connect 1/32" V-grooves on the inner surface of the steel, to the atmosphere. Gases driven out of the steel by heat were thus vented and the buckling of the inner copper lining avoided.

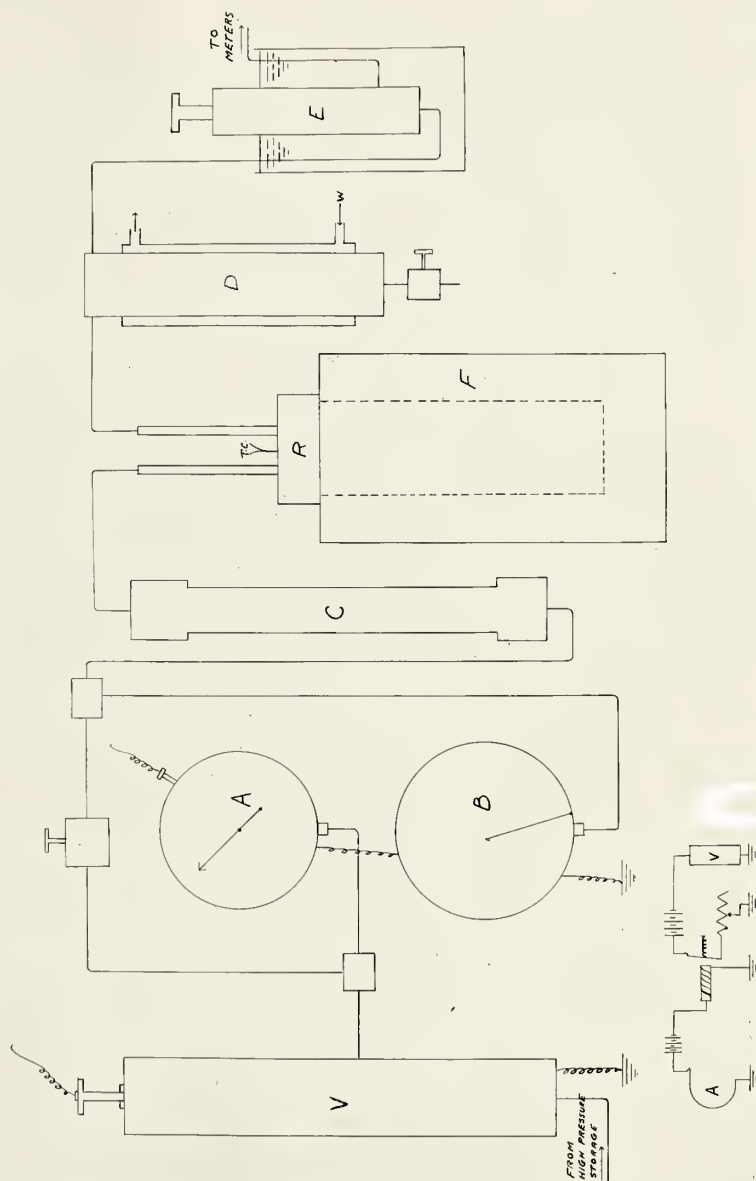
The catalyst chamber, C, was fitted with two perforated

distribution plates, top and bottom, to feed the gas uniformly throughout the catalyst mass. The gas inlet tube extended through the catalyst to below the lower distributing plate. A layer of asbestos was placed on top of the catalyst to prevent particles blowing out of the reactor into the condensing system on sudden pressure changes. The top and bottom copper plugs to the catalyst chamber were initially designed as shown by the top joint, but due to the exceedingly tight and almost immovable joint made by these contacts, both closures were latterly built as illustrated at the bottom plug. This arrangement made quite as satisfactory a joint from the standpoint of gas tightness, and was easily opened without undue effort.

Temperatures were read with an iron-constantan thermocouple. Control of this temperature was accomplished with a Leeds and Northrup potentiometer recorder-controller system, which usually held the temperature within 5° , although on occasions the range was $10-12^{\circ}$ when the voltage was irregular.

The arrangement of the apparatus is illustrated diagrammatically in figure 16. The pressure control system was that devised by Larsen and Karrer (153) and involves a relay actuated by a bourdon tube pressure gauge. The wiring circuit is illustrated in figure 16 and the operation is as follows. A standard hydraulic gauge was fitted with an insulated adjustable screw which made contact with the end of the bourdon tube at any de-

FIGURE 16



sired pressure. When the pressure in the system is below the required pressure, the relay closes the circuit through the solenoid in the regulating valve and this valve is opened admitting gas. When the pressure arrives at that desired, the bourdon tube makes contact with the screw and completes the gauge circuit which operates the relay and opens the solenoid circuit. A powerful spring forces the valve back into its seat shutting off the gas supply. The tension on the spring and the position of the solenoid are adjustable to allow operation against various differential pressures, and the pressure may usually be regulated to within 50 lbs. per sq. in. depending somewhat on the rate of flow of gases through the system.

In figure 16, V is the magnetic control valve, A is the controller gauge, of the standard bourdon tube type modified by the addition of the adjustable contact, and B is a recording gauge which gave a continuous record of the pressure changes. The gases next passed through a purifier, C, filled with activated charcoal to remove the iron carbonyl formed in the storage cylinder, tubing and apparatus preceding the reactor. This purifier was of bronze with steel caps fitted with bronze closure plugs. From this point the gases were carried through copper tubing, 5/16" O.D. by 1/8" I.D., to the autoclave, R, thence to a high pressure, water-cooled, bronze condenser, D. The valve, E, which served to reduce the pressure to atmospheric, was made

of duralumin body with a bronze stem. Thus the gases, after purification, did not come in contact with any ferrous material. The gases at atmospheric pressure passed through another condenser and the rate of flow was measured on a capillary flow-meter, following which the gases could be sampled before final measurement in a wet test meter filled with a mineral seal oil. No means were available of determining the initial volume of gas with precision.

Analytical Methods.

The general analyses necessary in this work were much the same as those previously outlined. Gases were analysed in the same manner, while liquids were fractionated in the column of Cooper and Fasce (152). Qualitative tests for organic compounds included the iodoform test for ketones and alcohols, while AgNO_3 was used to test for formic acid, and FeCl_3 for acetic acid in the absence of formic. Acetic acid was also noted quite readily by distillation.

Experimental Results.

The experiments to date have not yielded results worthy of very much consideration. The only method applicable in the present state of the science of catalysis may be described briefly as trial and error. The leads given by the previously detailed

work on the decomposition of ethyl alcohol were not very definite and showed primarily that the synthesis of ethyl alcohol would be a complex process. Considerable catalyst testing was carried out with the more favorable catalysts without any appreciable production of compounds more complex than methanol.

Very early in the high pressure work it was found that the catalysts developed at atmospheric pressure were not particularly useful and did not do more than indicate the basic types that might be of use. The majority of the work at present and in the future is on other catalysts developed in the light of the results obtained. The work is incomplete, being just out of the early stages, and is going forward. The complete testing of a catalyst under conditions of high temperature and pressure requires considerable time, averaging two weeks as compared to a few days at atmospheric pressure, and the periodic mechanical overhaul entails a further loss of time. In consequence the number of catalysts tested is small. The installation of at least one more testing set is advisable in order that a reasonable rate of tests be maintained.

The results to be reported are qualitative in the sense that the quantities of gas used are not known directly. They can be calculated approximately in some instances from the exit gases and liquids produced, but until they are measured directly a certain amount of uncertainty is attached to the yields.

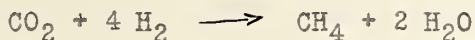
The small reactor described and illustrated in figure 15-I was not at all satisfactory, due to the formation of iron carbonyl. The reacting gases always diffused to the steel walls where reactions occurred leading to the formation of various products including carbonyls. As mentioned by Fischer (5) the escaping gases burned with a bright luminous flame which was due to the presence of iron carbonyl, but contrary to Fischer, who observed this phenomenon only at the commencement of an experiment, this unusual flame was characteristic for the duration of all reactions conducted with water gas in this reactor. The removal of considerable quantities of CO in this manner, and the deposition of Fe on the catalyst by the thermal decomposition $\text{Fe}(\text{CO})_5$, were probably responsible for the negative results obtained in most cases.

The first catalyst investigated was number 24, previously described, containing Zn, Cr and Cu. Runs were conducted at 360, 400 and 480°, and in all cases only a small quantity of water was obtained. When removed from the condenser the liquids were water white, but almost immediately became a dark brown, due to iron carbonyl decomposition which probably formed a hydrated ferric oxide.

Catalyst number 19, containing 2.5% chromium oxide, 0.5% cerium oxide and the balance iron oxide, produced a trace of oil at 350°, but only small quantities of water at 425° and 500°,

while an iron catalyst promoted with cerium also gave unsatisfactory results with hydrogen and carbon dioxide.

Catalyst number 27 containing Ni, Cr, and Fe was next investigated with hydrogen and CO₂ under a pressure of 1300 lbs. at 325°. 8 cu.ft. of gas passed out of the autoclave and 83 com. of water were produced. The initial gas was 58% hydrogen and 42% CO₂, and the exit gas contained 64% CH₄, 5% H₂ and 31% CO₂. Evidently the reaction



was favorably affected by this catalyst. Approximately 15 cu.ft. were converted to CH₄ and H₂O. At 425° the results were similar but the catalyst was not as active. A new sample of catalyst was reduced and tested at 275°, but the catalyst was apparently not active at this temperature.

The next catalyst studied was number 44, due to Audibert and Raineau. At 350 and 450° only reactions producing CO₂, CH₄ and water were occurring and not more than traces of other compounds appeared.

The first catalyst to produce results, and the last one tested in the small autoclave, was number 34 containing cobalt and zinc. At 400° and a pressure of 2400 lbs. a definite but small amount of methanol, 2 ccm. was isolated from a total condensate of 61.5 gms. obtained with 23 cu.ft. of gas. The efficiency is

very low even with regard to the total reaction products. The bulk of the water gas reacted to form CH_4 and CO_2 . At 500° there was no evidence of alcohol, and large quantities of carbonyl were formed.

The new autoclave illustrated in figure 15-II, and arranged as shown in figure 16, was then placed in service. A blank run using water gas at 400°C under 2000 lbs. pressure, with a very small space velocity, produced only a slight amount of water from 5 cu.ft. With carbon dioxide and hydrogen at 425° only a trace of water and slight CH_4 formation was evident. The extraordinarily small catalytic activity of pure copper with regard to the numerous reactions possible with mixtures of hydrogen and the oxides of carbon is strikingly exemplified by these results.

Catalyst number 37, normal zinc chromate, was tested at $300 - 325^\circ$ under 1500 lbs. pressure, but proved to be rather inactive, producing only 24 c.c. of liquid from 7 cu.ft. of gas. About half of this condensate was water and the rest a sharp smelling oil. This same catalyst at 465° produced a small amount of condensate which formed two layers. The catalyst on removal showed no traces of carbonization, but possessed a very peculiar odor.

An iron-cerium catalyst prepared by double precipitation of the hydroxides was investigated at 425° and 1600 lbs. pressure.

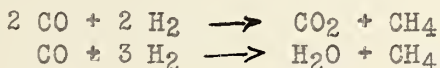
The iron promoted methane and water reactions primarily, but from 32 gms. of condensate 2.5 c.c. of an unidentified oil were obtained.

An equimolar mixture of iron and cobalt prepared by precipitation as the hydroxides, promoted methane and water formation at 300 - 350°.

The condensates with these catalysts still indicated the formation of small amounts of carbonyl, even when iron was not present in the catalyst, and at this stage the charcoal purifier previously described was placed in position before the autoclave.

The next catalyst studied with this arrangement was cobalt chromate. This catalyst was fairly active and favored the production of methane, water and CO₂ from water gas.

Two reactions obviously can occur



The equilibrium constants were calculated from the gas analyses and compared with the values calculated from the accepted free energy equations. Equilibrium was not attained in either case. At 350° a net flow of 7.5 cu.ft. produced 39 gs. of water, while the gas consisted of 21.8% CO₂, 55.1% CH₄, 20.9% H₂ and 2.2% CO. The results at 425° were similar with the exception that the condensate was quite blue in color and on acidification and distillation produced a few drops of acetic acid. Apparently acetic acid

was a product of the reaction and attacked the copper tubing.

The catalyst was next investigated with hydrogen and carbon dioxide. At 350°C definite indications of some low boiling constituents were obtained while qualitative tests for formic and acetic acids were positive, although the quantities were not very large. Similar results were obtained at 300° and an effort was made to determine some of the products present in the condensate by treatment with PCl_5 and isolation of the chlorides. The results of this treatment were not satisfactory, but small amounts of oils with boiling points corresponding to ethyl and isopropyl chlorides were obtained. An experiment at 300° with a gas rate of 600 ccm. per minute produced 6 gm. of condensate with 3.5 cu.ft. of gas, and at 350° and 1000 ccm. per minute, 14 gm. of liquid were obtained with the passage of 5.5 cu.ft. The liquid products were predominantly water.

Succeeding experiments at 350° with water gas showed that the catalyst was no longer active. Practically no liquid was obtained from 5 cu.ft. of gas. At 410°C, however, the methane and water producing reactions were again very prominent.

A new catalyst containing 4 moles of ZnO , 1 mole of Al_2O_3 and 1 mole of CuO was prepared by precipitation from a solution of the nitrates. This catalyst was excellent for the synthesis of methanol and was investigated in some detail. It was reduced with water gas and the observation was made that the liquid obtained on

reduction contained nearly 50% methanol which was rather a promising sign. The first run was made at 300° under 1650 lbs. pressure, 14.5 c.c. of methanol containing but a trace of water were obtained from a metered gas yield of 2 cu.ft. This run was made with water gas and the ultimate gas analysis indicated 8.4% CO₂, 55.0% H₂, 19.9% CO and 9.4% with a residue of 7.3% nitrogen. The efficiency was quite high but evidently appreciable reaction leading to CH₄ and CO₂ also occurred.

The reaction of CO₂ and H₂ over this catalyst is of interest in showing the ready conversion of such gas mixtures to methanol and water. Such results have not appeared to any extent in the literature and they are presented in detail in the following table.

The conversion of CO₂ and H₂ to MeOH and H₂O

Experiment No.	39	47	48
Pressure lbs/sq.in.	1600	2000	2100
Rate, cc/min.exit gas	50	125	300
Temperature °C	300	275	275
Condensate ccm.	6.5	8.0	26.5
Methanol ccm.	5.0	4.4	10
Gas, cu.ft.	2.4	4.0	15.4

Exit gas analysis

CO ₂	8.5	24.1	25.3
H ₂	77.8	72.1	69.5
CO	3.3	nil	nil
CH ₄	9.2	nil	3.1

The condensates were almost entirely methanol and water, but the balance between them is not very good, particularly in

Expt. #39. The lower temperature seems most favorable in view of the lack of side reactions leading to CO. Some methane appears in Expt. #48 which is surprising in view of the higher space velocity. The efficiency is fairly high, about 30% conversion in Expt. #39 and somewhat less in the other two. The catalyst loses its activity rapidly with continued use.

The action of water gas was again investigated at higher temperatures, 350°C, but owing either to the loss of activity of the catalyst or the effect of higher temperature, the results were not satisfactory. 2.5 cu.ft. of gas, passed at a rate of 75 ccm. per minute, produced only 2.2 c.c. of condensate, while at a flow of 300 ccm. per minute, 8.3 cu.ft. of gas gave 8 c.c. of liquid. These results correspond to a yield of only 0.88 and 0.75 ccm. of liquid per cu.ft. of gas, approximately 10% conversion. In both cases the product was practically pure methanol. The same catalyst was tested at 275° but produced only 4 ccm. of liquid from 6 cu.ft. of water gas, and of this 2.7 ccm. were methanol, the balance being water with a trace of oil.

A fresh sample of this catalyst was reduced with hydrogen. This produced a very satisfactory active catalyst, and at 300°C, 1600 lbs. pressure and a space velocity of 200, it produced 15.5 c.c. of liquid from 1.8 cu.ft. of gas. The space velocity is calculated on the basis of exit gas. 14.0 ccm. of this liquid were methanol and the balance water; 3.5% of the exit gases were methane.

This indicates 45% conversion to methanol in a single passage, which compares favorably with other results. Under similar conditions but a quadrupled space velocity of 800 the conversion was 33% with only a small amount of water produced. These figures represent respective yields of 6.8 and 5 cc. of liquid per cu.ft. of gas. At 275° and a space velocity of 500 a conversion of 45% was again obtained, and the condensate was 100% methanol. A much higher space velocity, 1000, at the same temperature reduced the yield to only 15% conversion.

A final run was made with water gas at 325°C and a space velocity of 800. The yield was not very large, only 1.2 cc. of methanol being obtained per cu.ft. of gas. The condensate, however, was pure methanol. The catalyst appears sensitive and loses its activity readily.

For comparative purposes these results with water gas are summarized below.

<u>Temperature °C</u>	<u>Space Velocity</u>	<u>Yield in cc. per cu.ft.</u>
275	500	8.6
275	1200	3.0
300	200	6.3
300	200	6.8
300	800	5.6
325	800	1.2
350	300	0.88
350	1200	0.75

Quite obviously the optimum temperature with this catalyst at a pressure of 1500-2000 lbs. is 275 - 300°. The marked decline

in activity above 300° was not totally unexpected but was very abrupt. The yield varies inversely with the space velocity but is not proportional as indicated by a comparison of the 300° runs.

The results with hydrogen and CO₂ indicate the possibility of developing a satisfactory catalyst from some Zn, Cu, Al mixture, but the yields with this sample were not large enough for successful application.

The production of methyl ether or ethanol has not been found to occur in appreciable amounts on the catalysts investigated. Presumably a catalyst that will favor the reactions leading to ethanol must possess dehydrating properties as well as those properties common to all successful methanol catalysts. Aluminum does not appear to supply the necessary factors to the catalyst. A series of catalysts have been prepared which possess a more powerful dehydrating action and have been partially investigated with water gas. They comprise the borates, phosphates and silicates of the metals commonly used in methanol synthesis. Those examined at this time are only slightly active and the main product is water containing small amounts of acids. The production of methane occurs by the reduction of both CO and CO₂. High temperatures, such as 400°C, are necessary for reaction, and in this region the decomposition of CO to C and CO₂ frequently occurs.

Summary.

At the present stage of this research it is difficult to draw any conclusions with regard to the results. The empirical nature of the methods of catalyst testing does not permit much speculation and involves a large amount of negative results. There does not appear to be any relation between the results of the decomposition of ethyl alcohol and the corresponding synthesis. With those catalysts and conditions utilized, two primary reactions occur, the production of methane and water or carbon dioxide, and the production of methanol.

No evidence of further reaction has been obtained other than a slight production of oil and acetic or formic acid in a few cases. Amounts of oxygenated organic compounds of less than 1% or 2% would escape detection. The complex series of reactions outlined in the literature does not appear to occur to any great extent. Methyl ether has not been found in any quantity even with a definitely dehydrating catalyst, which is not in line with the experience of others.

It has been shown that CO_2 and H_2 readily produce methanol on a suitable catalyst. This catalyst is also efficient in the production of methanol from CO and H_2 . This would suggest that there is a similarity between the two reactions involving probably in the first instance a primary reduction of CO_2 to CO .

P A R T I V.

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No claim is made for the completeness of this bibliography, but an effort has been made to include those which serve as guides to catalytic action and general high pressure work.

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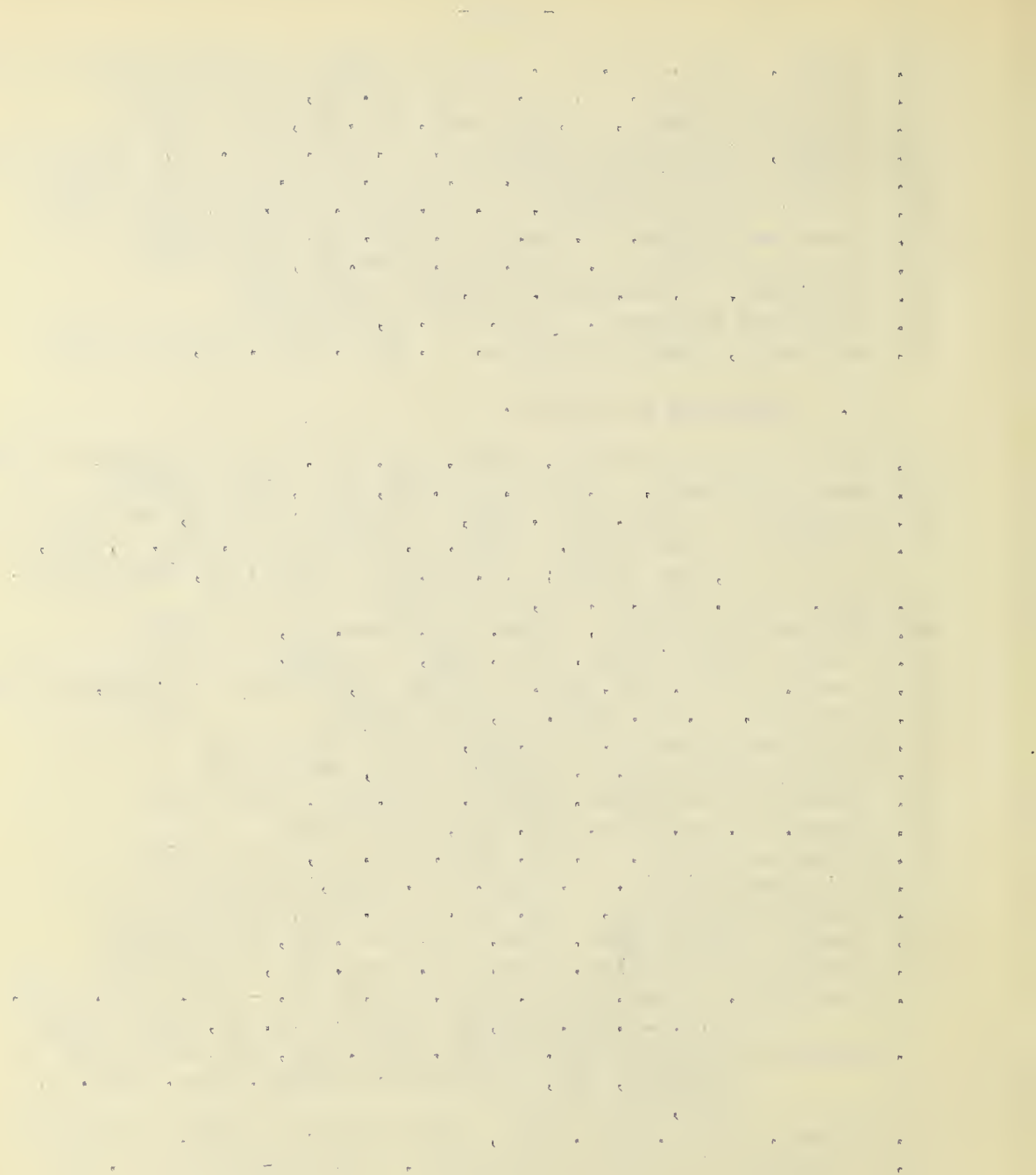
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